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Effects of Non-Photochemical Processes on the Meridional Distribution and Total Amount of Ozone in the Atmosphere

by

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ABSTRACT

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The photochemical equilibrium distribution of ozone below 41 km is computed for the solstices and equinoxes from recent rocket observations of the solar ultraviolet energy received at the top of the atmosphere.

In this study an attempt is made to investigate the important part played by the mean seasonal transport processes in distributing the ozone below 41 km in the stratosphere. To make such an investigation it is assumed that a steady state meridional distribution of ozone is produced when photochemical and transport processes are acting together. Relevant theory and numerical procedure to compute such a steady state meridional distribution of ozone have been developed.

In order to make a model of the transport processes that is needed for the calculation of the distribution of ozone, theoretical and observational information available at present on the various transport processes present in the stratosphere is reviewed. Further, in the calculations of ozone an attempt is made to combine the mean meridional motions and the large scale mixing processes within the limits acceptable to the current ideas on these transport processes.

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The seasonal distribution of total ozone thus computed from the model of the transport processes and with an assumption of steady state condition shows a satisfactory agreement with the observed seasonal and latitudinal variation of total ozone. The mean annual total ozone variation with latitude deduced from the computed seasonal distribution of total ozone, demonstrates the ability of the method developed here to account for the mean annual total ozone variation with latitude observed in the earth's atmosphere.

The model of the transport processes developed in this study to calculate the distribution of ozone in the atmosphere emphasizes the importance of the large scale eddy diffusion processes. The theoretical and observational findings from the spread of W^{185} (a radioactive isotope of tungsten introduced into the stratosphere by nuclear explosions) have been very useful in making this model of the transport processes.

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I. A. Introduction

Our knowledge of the distribution of ozone in the atmosphere is derived largely from the observations of the vertical distribution of ozone at comparatively few and widely scattered stations on the earth.

The Umkehr method (Götz, 1931) of obtaining the distribution of ozone was widely used until recently. From the Umkehr method standard curves of the vertical distribution of ozone[1] at a given station for different amounts of total ozone contained in a vertical column of unit area were constructed. Then, using the observed total amount of ozone at the station for any given day, the vertical distribution of ozone for the day was read off these standard curves. Ramanathan and Kulkarni (1960) have constructed the meridional distribution of ozone using such a technique on the data obtained at Kodaikanal, Poona, Mount Abu, Delhi, Srinagar, Tetano, Arosa, Tromsö, and College, Alaska. The models of the distribution of ozone given by Ramanathan and Kulkarni from the equator to 80°N latitude for November and July are combined as shown in Fig. 1 to yield a distribution of ozone from one pole to the other.

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[1]Vertical distribution of ozone is usually expressed in Dobson Units: D.U. = 10^{-3} cm of ozone at standard temperature and pressure. Also D.U. = 2.69×10^{18} molecules of ozone/cm^2.

Besides the Umkehr method there have been other methods developed to measure the vertical distribution of ozone. Regener (1954), using an ozone-sonde based on the principle of photographic photometry, has measured the vertical distribution of ozone at Albuquerque. Using the observations of the emission and absorption of infrared radiation by ozone in the 9.6μ band Epstein, et al. (1956) at Flagstaff, Arizona, and Goody and Roach (1956) at Oxford, England, have derived the vertical distribution of zone. Brewer (1960) has made measurements of the vertical distribution of ozone at Liverpool and Malta with a chemical ozone-sonde. It is very difficult to put together such measurements obtained by different methods and to make a model of the meridional distribution of ozone.

Very recently Paetzold and Piscalar (1961) using the observations of the vertical distribution of ozone made during the I.G.Y. with an optical radio ozone-sonde at four stations-- Tromsö, Weissenau, Leopoldville, and Denver-- have constructed a meridional distribution of ozone for spring and fall, which is presented here as Fig. 2.

Both these models of the "observed" meridional distribution of ozone, the construction of which could not be attempted until recently and still based on data collected from a few stations. Nevertheless, these models bring out the salient features of the atmospheric ozone.

Ozone is produced in the earth's atmosphere by the photochemical reactions induced by the solar ultraviolet radiation (Chapman, 1930). Although the photochemical reactions (referred to hereafter as photochemical theory) lead to the formation of ozone in the atmosphere, the observed global distribution of ozone cannot be completely explained on the basis of photochemical theory alone.

Total ozone computed from the photochemical theory is short of the observed total amounts at higher latitudes, and it is in excess of the amounts observed at the equatorial latitudes (Craig, 1950). Photochemical theory would lead to summer maximum and winter minimum of total ozone at all latitudes, while the observations show a maximum in spring and a minimum in autumn at high latitudes as shown in Fig. 3 (London, 1962). Small seasonal variations are observed at the equatorial latitudes (Ramanathan, 1954).

The vertical distribution of ozone concentration according to photochemical theory has a maximum at about 30 km height in the atmosphere, and the position of maximum is higher, the higher the latitude (Fig. 12). On the contrary, observations on the vertical distribution of ozone show that the position of the maximum is usually lower when the latitude is higher, leading to a lowering of the center of gravity of the ozone layer with increase in latitude (Fig. 4).

Photochemical studies made by previous investigators (see, e.g., Wulf and Deming, 1937; Craig, 1950; Dütsch, 1956) showed that the half-life of ozone was of the order of a day at heights above about 30 km, and that photochemical conditions could prevail above that level. However, below that level the production of ozone by solar ultraviolet rapidly decreased, and any departures from photochemical equilibrium conditions could persist for long periods of time. Arguing on such grounds to explain the seasonal and latitudinal variations of ozone, Craig suggested that there should be "some atmospheric process which transports ozone from regions where is can be quickly reformed (high levels or equatorial regions) to lower protected levels where it can persist." He further commented that ". . . this process must be most effective in middle and high latitudes in winter, when the total amount of ozone increases most rapidly."

Dütsch (1946) first made an attempt to introduce changes of ozone due to Austausch and circulation and to obtain a seasonal variation of ozone as a function of latitude. Craig (1950) remarked that the seasonal and latitudinal variations obtained by Dütsch were qualitatively similar to the observed ones, but of extremely small amplitude (about 20 percent of the observed latitudinal amplitude and about 5 to 10 percent of the observed seasonal amplitude at high latitudes).

B. Objective of the present study

From the earlier discussion it may be seen that transport

by advection and diffusion on different space and time scales plays a significant role in producing the geographical distribution of ozone. At present it is difficult to consider elaborately the effects of small scale phenomena owing to the lack of information on the nature of these transport process on small space and time scales in the stratosphere.

In this study it is intended to compute the photochemical distribution of ozone, using the best available data needed for such computations, as a function of latitude and season. This is done as a basic step before proceeding to examine the influence of transport processes on the distribution of ozone.

The measurements of total ozone in the atmosphere show clearly an annual cycle of the ozone variation with the largest and the least amounts in spring and fall respectively. The striking contrast between the mean seasonal ozone amounts in the atmosphere has been demonstrated by Ramanathan (1954) and London (1962). Such mean seasonal features of total ozone suggest that the part played by the mean seasonal transport processes in distributing the ozone in the lower stratosphere, where the bulk of ozone present is under weak solar control, could be of paramount importance. This influence of the mean seasonal transport processes on ozone in the lower stratosphere is probably capable of masking the direct influence of solar radiation, the ultimate source of ozone. Hence in this study it is intended to make an experiment on the calculation of the

meridional distribution of ozone produced under steady state condition by transport processes and solar radiation. Further, it is intended to see if such an approach can explain the seasonal variation of ozone in the earth's atmosphere.

In this study an attempt is made to develop the equations necessary for calculating the distribution of ozone in the atmosphere under steady state conditions when photochemistry is coupled with local change of ozone due to mean seasonal meridional motions and large scale mixing processes. Further, the numerical procedure to solve such equations will be developed.

Posing the problem of atmospheric ozone as a steady state or boundary value problem has a unique advantage, namely it is not necessary to specify the initial distribution of ozone in the atmosphere to get a steady state solution, so that the solution is not subject to the uncertainties of the initial distribution.

The mean seasonal transport processes in the stratosphere needed for this study will be deduced from the recent available observational and theoretical information.

II. Theory

A. Basic photochemistry of ozone

The photochemical reactions involved in producing the ozone layer below 50 km are (see, e.g., Craig, 1950; Dütsch, 1956):

$$O_2 + h\nu \rightarrow O_1 + O_1 \qquad (1)$$

($\lambda < 2400$ Å, oxygen absorption in Schumann Runge bands and Herzberg continuum)

$$O_1 + O_2 + M \xrightarrow{K_2} O_3 + M \qquad (2)$$

$$O_3 + O_1 \xrightarrow{K_3} 2O_2 \qquad (3)$$

$$O_3 + h\nu \rightarrow O_1 + O_2 \qquad (4)$$

($\lambda < 11000$ Å, ozone absorption in Hartely, Huggins and Chappuis bands)

where O_1, O_2, O_3, and M stand for number of atomic oxygen, molecular oxygen, ozone and total number of molecules per cm^3. Symbol h is the Planck's constant and ν, the frequency of radiation. K_2 (cm^6 $molec^{-2}$ sec^{-1}) and K_3 (cm^3 $molec^{-1}$ sec^{-1}) are the rate coefficients of the reactions (2) and (3).

The above four reactions give the rate of growth of O_1 and O_3 as

$$\frac{\partial O_1}{\partial t} = 2f_2O_2 + f_3O_3 - K_2O_1O_2M - K_3O_1O_3 \qquad (5)$$

$$\frac{\partial O_3}{\partial t} = -f_3O_3 + K_2O_1O_2M - K_3O_1O_3 \qquad (6)$$

where f_2 and f_3 stand for the number of quanta of energy absorbed per second per molecule of oxygen and ozone.

Under equilibrium conditions

$$\frac{\partial O_1}{\partial t} = \frac{\partial O_3}{\partial t} = 0 \qquad (7)$$

With the above condition we have from (5)

$$O_1 = (2f_2O_2 + f_3O_3) / (K_2O_2M + K_3O_3) \qquad (8)$$

Substituting for O_1 from (8) into (6) (and neglecting O_3 in comparison to $\frac{K_2}{K_3}O_2M$) we get the photochemical equilibrium ozone, O_{3e}

$$O_{3e} = O_2\sqrt{\frac{K_2 f_2 M}{K_3 f_3}} \qquad (9)$$

B. Effects of transport processes

1. General considerations. The photochemical equations are developed by considering only the solar radiation and its direct influence on the atmosphere. However, if transport processes such as advection and diffusion are present in the atmosphere, they tend to redistribute the ozone produced by solar radiation. In such a redistribution, regions of the atmosphere where photochemical production of ozone is rapid act like sources,

and regions where the photochemical production is weak constitute sinks of ozone.

Before introducing the effects of transport processes into the growth equation for ozone, it is intended to develop basic ideas necessary for such a study by considering the influence on ozone of an external input at the rate of F molecules of O_3/cm^3-sec. The growth equation (7) for ozone now becomes

$$\frac{\partial O_3}{\partial t} = -f_3 O_3 + K_2 O_2 O_1 M - K_3 O_3 O_1 + F \qquad (10)$$

Substituting for O_1 from (3) into (10), we have

$$\frac{\partial O_3}{\partial t} = -f_3 O_3 + \{K_2 O_2 M - K_3 O_3\} \frac{(2f_2 O_2 + f_3 O_3)}{(K_2 O_2 M + K_3 O_3)} + F \qquad (11)$$

We divide the above equation by $K_3 O_3$ and write N_3^* for $K_2 O_2 M/K_3$ and get

$$\frac{\partial O_3}{\partial t}\left[\frac{N_3^*}{O_3} + 1\right] = -2f_3 O_3 + F\left[1 + \frac{N_3^*}{O_3}\right] + 2f_2 O_2 \left[\frac{N_3^*}{O_3} - 1\right] \qquad (12)$$

Now the external input at the rate of F molecules of O_3/cm^3-sec and the photochemical process tend to a new equilibrium of ozone O_{3E} given by (13), when $\frac{\partial O_3}{\partial t} = 0$:

$$2f_3O_{3E} - F\{1 + \frac{N_3^*}{O_{3E}}\} - 2f_2O_2\{\frac{N_3^*}{O_{3E}} - 1\} = 0 \quad (13)$$

Since $\frac{N_3^*}{O_{3E}} >> 1$, as was stated in arriving at equation (9), we can write equation (13) as

$$2f_3O_{3E} - F\frac{N_3^*}{O_{3E}} - 2f_2O_2\frac{N_3^*}{O_{3E}} = 0 \quad (14)$$

or

$$O_{3E} = \sqrt{\frac{(F + 2f_2O_2)}{2f_3}N_3^*} \quad (15)$$

Dütsch (1946) first arrived at this equation. Equation (15) may be transformed with the help of equation (12) as

$$O_{3E} = O_{3e}\sqrt{1 + \frac{F}{2f_2O_2}} \quad (16)$$

Equation (16) shows that an input of F molecules of O_3/cm^3-sec does not indefinitely increase the amount of ozone, for solar radiation exerts a control on the growth of ozone so that a new equilibrium is reached which is related to the photochemical equilibrium O_{3e} and to the ratio $F/2f_2O_2$.

Similarly from (16) it may further be inferred that $O_{3f} < O_{3e}$ when F is negative. However, when F is negative, a scrutiny of equation (16) shows that there is no real solution for O_{3f} if $(2f_0 O_3 + F) < 0$. This condition can be overcome by the following physical considerations.

Until now F was considered only as a positive or negative rate of input for developing the basic equations. However, in the atmosphere local rate of change of ozone due to advective and diffusive processes results from the spatial distribution of ozone and the relative intensities of these transporting agencies. Thus, under equilbrium conditions, the spatial distribution assumed by ozone will be such that at each point in the field, flux convergence or divergence of ozone is in balance with the photochemical destruction or production of ozone at that point. On physical grounds it becomes untenable to obtain a field of ozone under steady state that has flux divergence at any point in the field over and above photochemical production at that point.

2. Transport by large scale diffusion and mean meridional motions. We may now proceed to introduce the changes of ozone due to large scale diffusion and mean meridional motions in the growth equation (12). However, to take into account the variation of density in the atmosphere we have to choose a property of ozone that is a

function of the atmospheric density. Such a property of ozone is its mixing ratio

$$\chi = \frac{O_3 \text{ molecules/cm}^3}{\text{air molecules/cm}^3}$$

Thus

$$O_3 = M\chi \tag{17}$$

Now the rate at which ozone increases at any given point per unit volume per unit time, due to a velocity $\mathbb{V}$ is given by the equation of continuity for ozone.

$$\left[\frac{\partial(M\chi)}{\partial t}\right]_a = -\nabla\cdot(M\chi\mathbb{V}) \tag{18}$$

The subscript a refers to air motions.

Now let u, v, and w be the components of $\mathbb{V}$ along x the east, y the north, and z the vertical directions. Expressing these velocity components and χ in terms of their mean and turbulent part we have

$$\begin{aligned}
\chi &= \overline{\chi} + \chi' \\
\mathbb{V} &= \overline{\mathbb{V}} + \mathbb{V}' \\
u &= \overline{u} + u' \\
v &= \overline{v} + v' \\
w &= \overline{w} + w'
\end{aligned} \tag{19}$$

where the time averaged quantities $\bar{\chi}$, $\bar{\mathbb{V}}$, $\bar{u}$, $\bar{v}$, and $\bar{w}$ are defined as

$$(\overline{\qquad\qquad}) = \frac{1}{\tau}\int_0^{\tau} (\qquad)dt \tag{20}$$

τ is a period comparable to the length of a season. Thus

$$[\frac{\partial(M\chi)}{\partial t}]_a = -\nabla\cdot[M(\bar{\chi} + \chi')(\bar{\mathbb{V}} + \mathbb{V}')] \tag{21}$$

that is,

$$[\frac{\partial(M\chi)}{\partial t}]_a = -\nabla\cdot(M\bar{\chi}\bar{\mathbb{V}}) - \nabla\cdot(M\bar{\chi}\,\mathbb{V}') - \nabla\cdot(M\chi'\bar{\mathbb{V}}) - \nabla\cdot(M\chi'\mathbb{V}') \tag{22}$$

Let $\bar{M} = M$. Then averaging over time would give

$$[\frac{\partial(M\chi)}{\partial t}]_a = -\nabla\cdot(M\bar{\chi}\bar{\mathbb{V}}) - \nabla\cdot(M\overline{\chi'\mathbb{V}'})$$

$$= -\bar{\mathbb{V}}\cdot\nabla(M\bar{\chi}) - M\bar{\chi}\nabla\cdot\bar{\mathbb{V}} - \nabla\cdot(M\overline{\chi'\mathbb{V}'}) \tag{23}$$

$$\therefore [M\frac{\partial\bar{\chi}}{\partial t} + \bar{\chi}\frac{\partial M}{\partial t}]_a = -M\bar{\mathbb{V}}\cdot\nabla\bar{\chi} - \bar{\chi}\,\bar{\mathbb{V}}\cdot\nabla M - M\bar{\chi}\nabla\cdot\bar{\mathbb{V}} - \nabla\cdot(M\overline{\chi'\mathbb{V}'}) \tag{24}$$

Now, from the qeuation of continuity we have

$$\frac{1}{M}\frac{dM}{dt} = -\nabla\cdot\bar{\mathbf{V}} \tag{25}$$

$$\therefore \bar{\chi}\left(\frac{\partial M}{\partial t} + \bar{\mathbf{V}}\cdot\nabla M\right) + M\bar{\chi}\nabla\cdot\bar{\mathbf{V}} = 0 \tag{26}$$

and so

$$\left[\frac{\partial\bar{\chi}}{\partial t}\right]_a = -\bar{\mathbf{V}}\cdot\nabla\bar{\chi} - \frac{1}{M}\nabla\cdot(M\overline{\chi'\mathbf{V}'}) \tag{27}$$

When we expand $\bar{\mathbf{V}}$ and $\mathbf{V}'$ into their components we get

$$\left[\frac{\partial\bar{\chi}}{\partial t}\right]_a = -\left(\bar{u}\frac{\partial\bar{\chi}}{\partial x} + \bar{v}\frac{\partial\bar{\chi}}{\partial y} + \bar{w}\frac{\partial\bar{\chi}}{\partial z}\right) - \frac{1}{M}\left\{\frac{\partial}{\partial x}M\overline{\chi'u'} + \frac{\partial}{\partial y}M\overline{\chi'v'} + \frac{\partial}{\partial z}M\overline{\chi'w'}\right\} \tag{28}$$

We further assume zonal symmetry of $\bar{\chi}$ and a steady zonal wind $\bar{u}$, and we can reduce equation (28) to

$$\left[\frac{\partial\bar{\chi}}{\partial t}\right]_a = -\left(\bar{v}\frac{\partial\bar{\chi}}{\partial y} + \bar{w}\frac{\partial\bar{\chi}}{\partial z}\right) - \frac{1}{M}\left\{\frac{\partial}{\partial y}M\overline{\chi'v'} + \frac{\partial}{\partial z}M\overline{\chi'w'}\right\} \tag{29}$$

The term $-\left(\bar{v}\frac{\partial\bar{\chi}}{\partial y} + \bar{w}\frac{\partial\bar{\chi}}{\partial z}\right)$ in (29) expresses the local change of χ at any given point in the meridional plane due

to mean meridional and vertical motions.

The terms $-\frac{\partial}{\partial y} M\overline{x'v'}$ and $-\frac{\partial}{\partial z} M\overline{x'w'}$ in (29) may be transformed with the help of the Austausch assumption (see, for example, Haurwitz 1941) of diffusion as

$$-\frac{\partial(M\overline{x'v'})}{\partial y} = \frac{\partial}{\partial y}\left[MKy \frac{\partial \bar{\gamma}}{\partial y}\right]$$

and

$$-\frac{\partial(M\overline{x'w'})}{\partial z} = \frac{\partial}{\partial z}\left[MKz \frac{\partial \bar{\gamma}}{\partial z}\right] \tag{30}$$

where K_y and K_z (cm^2/sec) are the eddy diffusion coefficients along the y and z directions. Upon neglecting the variation of density, M along y, the local change of ozone at a given point due to large scale diffusion and mean meridional motions may be obtained from (29), (30), and (17), as

$$\left[M \frac{\partial \bar{\gamma}}{\partial t}\right]_a = -M\left(\bar{v} \frac{\partial \bar{\gamma}}{\partial y} + \bar{w} \frac{\partial \bar{\gamma}}{\partial z}\right) + M\left[Ky \frac{\partial^2 \bar{\gamma}}{\partial y^2} + \frac{\partial Ky}{\partial y} \frac{\partial \bar{\gamma}}{\partial y} + Kz \frac{\partial^2 \bar{\gamma}}{\partial z^2} + \frac{\partial Kz}{\partial z} \frac{\partial \bar{\gamma}}{\partial z} + Kz \frac{1}{M} \frac{\partial M}{\partial z} \frac{\partial \bar{\gamma}}{\partial z}\right] \tag{31}$$

If we substitute for P, in equation (13), the local change of ozone $M\left[\frac{\partial \bar{\gamma}}{\partial t}\right]_a$ from (31) and then divide by $\left(\frac{O_{3\varepsilon} + N_3^*}{O_{3\varepsilon}}\right)$, we obtain

$$-2f_3 \frac{O_{3\varepsilon}^2}{N_3^* + O_{3\varepsilon}} + 2f_2 O_2 \left[\frac{N_3^* - O_{3\varepsilon}}{N_3^* + O_{3\varepsilon}}\right] + \left[M \frac{\partial \bar{\gamma}}{\partial t}\right]_a = 0 \tag{32}$$

or

$$- 2 \frac{f_2}{M} \frac{(M\bar{\chi})^2}{(N_3^* + M\bar{\chi})} + 2 f_2 \frac{O_2}{M} \left[\frac{N_3^* - M\bar{\chi}}{N_3^* + M\bar{\chi}}\right] + \left[\frac{\partial \bar{\chi}}{\partial t}\right]_a = 0 \qquad (33)$$

Equation (33) describes the combined effects of the photochemical and transport processes under steady state conditions. By solving (33) for $\bar{\chi}$ as a function of latitude and height we can get the distribution of $\bar{\chi}$ and hence $O_{3\varepsilon}$ in the meridional plane.

The numerical methods and boundary conditions necessary to solve equation (33) are discussed in the next section.

During the polar night in the winter hemisphere there is no dissociation of oxygen or ozone by radiation. Hence the local change of ozone at any point under such conditions will be entirely due to transport processes. It is also possible that air motions could transport atomic oxygen into the polar night. Such transported atomic oxygen could form ozone in the polar night through reaction (2). Kellogg (1961) has demonstrated by his calculations the importance of such transported atomic oxygen in heating the layers of the atmosphere above 80 km. However, at lower levels below about 40 km, it is reasonable to assume, following Craig (1950), that O_1 is used up in the reaction (2) in situ, so that the O_1 transport may be neglected.

III. Procedure of the investigation

A. Discussion of the data used.

It is necessary to have data on the solar energy received at the top of the atmosphere, the absorption coefficients of oxygen and ozone, the temperature and density distribution in the atmosphere, and the reaction rate coefficients K_2 and K_3 in order to calculate the vertical distribution of ozone in the atmosphere.

From the most recent rocket measurements of the solar spectrum we have now very reliable estimates of the energy in the ultraviolet radiation received at the top of the atmosphere. The two measurements of the solar ultraviolet spectrum, one reported by Detwiler *et al.* (1961) and the other by Hinteregger (1961) agree with one another quite well. The value of the solar ultraviolet energy received at the top of the atmosphere from 1800 to 2600 Å used in this study are taken from measurements of Detwiler *et al.* Above 2600 Å the solar radiation received at the top of the atmosphere tabulated by Gast (1960) is adopted. The solar spectrum thus constructed is shown in Fig. 5.

Watanabe *et al.* (1953), using vacuum ultraviolet technique, measured the absorption coefficients of oxygen between 1050 and 1900 Å. The absorption coefficients of oxygen in the Schumann-Runge bands from 1800 to 1900 Å

are adopted from the measurements reported, independent of pressure, by these investigators. However, they point out that their results show a pressure variation of the coefficients by a factor of 4 to 5 in the absorption peaks, and 2 to 3 in the absorption minima. In view of the apparent pressure dependency of the "observed coefficients" reported by them, they remark that their "data were smoothed somewhat arbitrarily, i.e., low pressure data were used for maxima, and high pressure data for minima" to obtain absorption coefficients of oxygen independent of pressure.

Heilpern (1952) showed that the absorption coefficient of oxygen is pressure dependent in the region 2100 to 2400 Å. In his measurements he used eight different pressures (between 50 and 127 kgms/cm^2) to obtain the functional form of pressure dependency of the extinction coefficients for a mixture of oxygen and nitrogen having a composition similar to air. Samples of air gave the same results within the accuracy of his experimental values. He fitted his results for the entire region to an equation of the form

$$\epsilon p = \epsilon_1 P_1 + \epsilon_2 P_2 + \epsilon_3 P_1 P_2$$

where $\epsilon(cm^{-1})$ is the extinction coefficient, P_1(kgms/cm^2) is the partial pressure of oxygen, P_2(kgms/cm^2) is the

partial pressure of nitrogen, and ϵ_1, ϵ_2 and ϵ_3 are coefficients evaluated by fitting the data to the above equation.

Heilpern's investigation of the extinction coefficient of a similar mixture in the pressure range 0.2 to 130 kgm/cm^2 and at 2144 Å agreed with the functional form obtained from the whole region 2100 Å to 2400 Å. On the strength of the observations at 2144 Å, which were extended to the lower pressure range, this form of pressure dependency is accepted in this work to hold good at low pressure for the entire region 2100 to 2400 Å. The absorption coefficients at pressures below 0.2 kgm/cm^2 encountered in the atmosphere, are obtained by extrapolating the experimental data with the help of the above functional form of pressure dependency.

The absorption coefficient of oxygen for the region 1900 to 2100 Å, lying between the limits of the experimental studies of Watanabe et al., and Heilpern, were obtained by interpolation. The interpolation was made at each desired pressure in the atmosphere.

The absorption coefficient of oxygen thus obtained at sea level pressure is compared in Fig. 6 with that of Craig (1950).

Vassy (1941) determined the absorption coefficients of ozone from 2020 Å to 2170 Å using ozonized oxygen and a photographic photometric method. However, she used Ny and Choong's (1933) value of the absorption coefficient

of ozone in the Huggins bands to measure the path length of ozone in her experiment.

Absorption coefficients of ozone in the region 1050 to 2200 Å were measured by Tanaka, Inn, and Watanabe (1954) using a vacuum ultraviolet technique. Their curve for the absorption intensity showed a minimum at about 2015 Å. They used pure ozone obtained by vaporizing liquid ozone instead of the ozonized oxygen used by the earlier experimenters. Tanaka, et al., however, remarked that "the results of Vassy, and Ny and Choong who measured down to 2020 Å and 2135 Å respectively are somewhat higher than the present data. The difference was about 10 percent at 2200 Å and about 40 percent at 2020 Å as compared to the data reported by Vassy. The discrepancies are greater than can be explained by ordinary experimental errors, and might be due to their use of the ozonized oxygen and photographic detection as opposed to the use of purer ozone and photoelectric detection."

But Tanaka et al., have observed chemiluminescence of pure ozone in their experiment. It is possible that the presence of such chemiluminescence of pure ozone in the investigation of Tanaka et al., may have been responsible for somewhat smaller values of the absorption coefficients of ozone.

As an extension to the measurements made by Tanaka et al., Inn and Tanaka (1953) measured the ozone absorption

in the near ultraviolet from 2000 to 3500 Å and in the visible region from 4000 to 7000 Å.

Vigroux (1953) studied the absorption of ozone in the Hartley, Huggins, and Chappuis bands using photographic photometric method and ozonized oxygen. He also studied the temperature dependency of the absorption coefficient of ozone. However, his observations do not extend to wavelengths shorter than 2300 Å in the Hartley bands.

Gast (1960) has tabulated the absorption coefficients of ozone from 2000 to 3000 Å determined by Inn and Tanaka. For the region 3000-3500 Å he has listed the absorption coefficients measured by Vigroux which he remarks are "recommended" by Inn and Tanaka. Gast has presented the absorption coefficients of ozone at 18°C and also (suitably applying the temperature correction given by Vigroux) at -44°C. The value corresponding to -44°C is better suited to calculate transmission of solar energy in the atmosphere.

In the present study the absorption coefficients of ozone at wavelengths longer than 2200 Å are adapted from the tables presented by Gast as shown in Fig. 7A. At wavelengths shorter than 2200 Å there is apparently a large difference between the absorption coefficients obtained by Tanaka et al., using pure ozone, and Vassy who used ozonized oxygen.

In this study the absorption coefficients of Vassy in the spectral region 2020 to 2200 Å have been adopted after reducing them by 10 percent to be consistent with the measurements of Inn et al., at 2200 Å. The absorption curve thus constructed after Vassy between 2020 and 2200 Å is then extrapolated to agree with that of Tanaka et al., at 1800 Å as shown in Fig. 7B.

Temperature and density distributions for the solstices are taken from Murgatroyd (1957) as a function of altitude and latitude. The value of the temperature and density below 16 km, the lowest level given by Murgatroyd, are obtained from the investigations of London et al., (1956).

The reaction rate coefficients K_2 and K_3 are adopted from Campbell and Nudelman's (1960) least square analysis of Glissmann and Schumacher's (1933) data on thermal decomposition of ozone in the temperature range from 70-110°C. According to Campbell and Nudelman, the functional form of K_2 and K_3 is given by

$$K_2 = 1.87 \times 10^{14} \text{ Exp } 1.49 \times 10^{3}/T \quad cm^6 gm\ mol^{-2} sec^{-1}$$

$$K_3 = 5.44 \times 10^{12} \text{ Exp } - 2.133 \times 10^{3}/T \quad cm^3 gm\ mol^{-1} sec^{-1}$$

The ratio of these two coefficients K_2/K_3 is compared in Fig. 8 with that obtained by Eucken and Patat (1936) in

their study on the temperature dependence of the photochemical formation of ozone. The logarithm of the ratio K_2/K_3, when plotted against 1/T, where T is the temperature in ^{o}K, gives a straight line as shown in Fig. 8.

B. Method of obtaining the meridional distribution of ozone when transport processes are present

Solution of equation (33) gives us the meridional distribution of $\bar{\gamma}$ and hence of ozone. To solve (33) the following numerical procedure is adopted.

The meridional plane from pole to pole and between 41 km to the height of the tropopause is divided into a grid, the gridpoints in which are spaced 10^{o} of latitude apart horizontally, and 2 km apart vertically as shown in Fig. 9. The boundary at 41 km representing the layer 42 to 40 km is chosen for the reason that ozone is reasonably undisturbed from its photochemical equilibrium at and above this level.

The boundary conditions used to solve (33) are:

(1) The flux of ozone through the vertical boundaries at the poles is zero.

(2) Photochemical equilibrium is assumed at 41 km, the upper boundary. However, during the polar night in the winter hemisphere, it is assumed that from 60^{o} to the pole the photochemical equilibrium is constant at 41 km.

(3) On the lower boundary at the tropopause level, the value of the ozone concentration is specified from the "observed" model of the meridional distribution of ozone given by Paetzold and Piscalar (1961).

The boundary condition (1) is purely a mathematical constraint and does not call for any knowledge of the distribution of ozone along the verticals at the poles. The boundary condition (2) at the 41 km level is quite justified from considerations of the photochemical theory, while the boundary condition (3) lacks the rigor of the preceding two conditions, and hence is subject to question. Further discussion of the boundary condition (3) is presented in the results.

The complete form of equation (33), after expansion of the term $[\frac{\partial \bar{\gamma}}{\partial t}]_a$, is seen to be

$$- \frac{2f_3}{M} \frac{(M\bar{\gamma})^2}{(N_3^* + M\bar{\gamma})} + 2f_2 \frac{O_2}{M} \left[\frac{N_3^* - M\bar{\gamma}}{N_3^* + M\bar{\gamma}}\right] - \left(\bar{v} \frac{\partial \bar{\gamma}}{\partial y} + \bar{w} \frac{\partial \bar{\gamma}}{\partial z}\right)$$

$$+ \left(Ky \frac{\partial^2 \bar{\gamma}}{\partial y^2} + \frac{\partial Ky}{\partial y} \frac{\partial \bar{\gamma}}{\partial y} + Kz \frac{\partial^2 \bar{\gamma}}{\partial z^2} + \frac{\partial Kz}{\partial z} \frac{\partial \bar{\gamma}}{\partial z} + Kz \frac{1}{M} \frac{\partial M}{\partial z} \frac{\partial \bar{\gamma}}{\partial z}\right) = 0 \qquad (34)$$

$\bar{\gamma}$, the ozone mixing ratio at each gridpoint, is calculated implicitly from equation (34). Numerical integration of the

above equation is performed at each gridpoint starting from 80° latitude in one hemisphere at the upper boundary, and proceeding downward along the vertical to the lower boundary, and then recommencing at the upper boundary at the next latitude, and so on until 80° latitude in the other hemisphere is reached

The parameters f_2 and f_s at each gridpoint depend on the solar energy reaching that point. However solar energy transmitted to any given height in the atmosphere is a function of the zenith angle of the sun. In order to simplify the calculations it is assumed that the sun radiates at a mean zenith angle [i.e., ½ (zenith angle at sun rise + zenith angle at noon)] corresponding to the given latitude and season. Further, to take into account the variation of the length of day, f_2 and f_s at each gridpoint are multiplied by the ratio, (daylight hours/24 hours), corresponding to each given latitude and season.

The finite difference scheme adopted here to solve (34) involves the central difference approximation to the second order space derivatives. For the first order space derivatives arising from advective terms, the Lelevier (Richtmyer, 1957) method of approximation is used. The basic idea behind Lelevier's method is to get the advection from the windward side of the gridpoint using non-centered differences.

The finite difference approximations to the various terms in (34) are written below with the help of Fig. 10.

All of the parameters χ, M, v, w, K_Y, and K_Z, are subscripted with the numbers 1, 2, 3, or 4 denoting the value of the parameter at the respective gridpoints in Fig. 10. The value of any of these parameters denoted without a subscript refers to the central point.

Further, we denote the horizontal velocity v as positive in the y direction pointing to the north. Similarly, the sign of the vertical velocity w is taken positive when directed upward along z.

$$- \overline{v} \frac{\partial \overline{\chi}}{\partial y} \begin{cases} \cong - v \dfrac{(\chi - \chi_4)}{\Delta y}, & (v > 0) \\ \cong - v \dfrac{(\chi_3 - \chi)}{\Delta y}, & (v < 0) \end{cases} \tag{35}$$

$$- \overline{w} \frac{\partial \overline{\chi}}{\partial z} \begin{cases} \cong - w \left(\dfrac{M - M_2}{2M}\right) \dfrac{\chi - \chi_2}{\Delta z}, & (w > 0) \\ \cong - w \left(\dfrac{M + M_1}{2M}\right) \dfrac{(\chi_1 - \chi)}{\Delta z}, & (w < 0) \end{cases} \tag{36}$$

The coefficients $\frac{M + M_2}{2M}$ and $\frac{M + M_1}{2M}$ in (36) arise due to the variation of density along z.

$$Ky\,\frac{\partial^2\bar{\chi}}{\partial y^2} \cong Ky\,\frac{\chi_2 + \chi_4 - 2\chi}{(\Delta y)^2}$$

$$\frac{\partial Ky}{\partial y}\,\frac{\partial\bar{\chi}}{\partial y} \cong \frac{(Ky_2 - Ky_4)}{(2\Delta y)}\,\frac{(\chi_2 - \chi_4)}{(2\Delta y)} \qquad (37)$$

$$Kz\,\frac{\partial^2\bar{\chi}}{\partial z^2} \cong Kz\,\frac{\chi_1 + \chi_3 - 2\chi}{(\Delta z)^2}$$

$$\frac{\partial Kz}{\partial z}\,\frac{\partial\bar{\chi}}{\partial z} \cong \frac{(Kz_1 - Kz_3)}{(2\Delta z)}\,\frac{(\chi_1 - \chi_3)}{(2\Delta z)}$$

$$Kz\,\frac{1}{M}\,\frac{\partial M}{\partial z}\,\frac{\partial\bar{\chi}}{\partial z} \cong Kz\,\frac{M_1 - M_3}{2M\Delta z}\,\frac{(\chi_1 - \chi_3)}{2\Delta z} \qquad (38)$$

With the finite difference approximations (35) to (38) we can transform equation (34) into an equation for χ at the central gridpoint.

$$\chi = \{2f_2\,\frac{O_2}{M}\,[\frac{N_2^* - M\chi}{N_3^* + M\chi}] + Ky\,\frac{\chi_2 + \chi_4}{(\Delta y)^2} + \frac{(Ky_2 - Ky_4)}{2\Delta y}\,\frac{(\chi_2 - \chi_4)}{2\Delta y}$$

$$+ Kz\,\frac{\chi_1 + \chi_3}{(\Delta z)^2} + \frac{(Kz_1 - Kz_3)}{2\Delta z}\,\frac{(\chi_1 - \chi_3)}{2\Delta z} \qquad (39)$$

$$+ Kz\,[\frac{M_1 - M_3}{2M\Delta z}]\,\frac{(\chi_1 - \chi_3)}{2\Delta z} + v\,\frac{\chi_4}{\Delta y} + w\,[\frac{M + M_3}{2M}]\,\frac{\chi_3}{\Delta z}\}$$

$$\div \{2f_3\,\frac{M\chi}{N_3^* + M\chi} + \frac{v}{\Delta y} + \frac{w}{\Delta z}\,[\frac{M + M_3}{2M}] + 2\,\frac{Kz}{\Delta z^2} + 2\,\frac{Kv}{\Delta y^2}\}$$

Equation (39) is solved by successive approximations to the value of χ. For example, the first guess to χ, let us say, is χ'. Then substituting χ' in the right-hand side of (39), we calculate a new value for χ denoted χ''. Now the new guess for χ, namely χ''', is obtained from

$$\chi''' = \frac{\chi' + \chi''}{2} \tag{40}$$

Successive approximations to χ are made until the criterion

$$\left|1 - \frac{\chi''}{\chi'}\right| \leq 0.02 \tag{41}$$

is satisfied. After the criterion (41) is satisfied, the ozone concentration ($M\chi$) at the center of the layer is obtained.

The boundary conditions (2) and (3) do not present any problem since they are specified to start with. But the boundary condition (1) has to be satisfied implicitly whenever equation(39) is being solved along the vertical at 80°N or 80°S latitude. This is achieved by solving equation (39) with the condition that, in any layer, χ at 80° latitude is equal to χ at the pole. In other words, along the vertical at 80° latitude, we solve the equation,

$$\chi = \{2f_2 \frac{O_2}{M} [\frac{N_3^* - Mx}{N_3^* + Mx}] + Ky \frac{\chi_4}{\Delta y^2} + \frac{(Ky_2 - Ky_4)}{2\Delta y} \frac{(\chi_2 - \chi_4)}{2\Delta y}$$

$$+ Kz \frac{\chi_1 + \chi_3}{\Delta z^2} + \frac{(Kz_1 - Kz_3)}{2\Delta z} \frac{(\chi_1 - \chi_3)}{2\Delta z}$$

$$+ Kz \frac{(M_1 - M_3)}{2M\Delta z} \frac{(\chi_1 - \chi_3)}{2\Delta z} + v \frac{\chi_4}{\Delta y} + w[\frac{M + M_3}{2M}] \frac{\chi_3}{\Delta z}\} \div$$

$$\{2f_3 \frac{Mx}{N_3^* + Mx} + \frac{v}{\Delta y} + \frac{w}{\Delta z} [\frac{M + M_3}{2M}] + 2 \frac{Kz}{\Delta z^2} + \frac{Ky}{\Delta y^2}\} \qquad (42)$$

Equation (42) is applicable at 80°N latitude. A similar equation for 80°S can be easily obtained by substituting $Ky \frac{\chi_2}{\Delta y^2}$ for $Ky \frac{\chi_4}{\Delta y^2}$ in the numerator of the right-hand side of (42).

After the entire field from 80°S to 80°N has been scanned by equations (39) and (41), a fresh iteration of the whole field is started again from 80°S. The whole field is then iterated several times until the values of χ or $O_{3\varepsilon}$ at any point in the whole field from two successive iterations do not differ by more than 1 percent. . .that is, if the value of χ is $[\chi]_1$ at any given point from preceding iteration, and $[\chi]_2$ from the succeeding iteration, the convergence criterion requires

$$|1 - \frac{[\chi]_2}{[\chi]_1}| < 0.01 \qquad (43)$$

To solve equation (39) and to obtain the steady state distribution of ozone corresponding to either the time of solstices or equinoxes, we do not have to specify the distribution of ozone in the interior of the field. One may start with the photochemical equilibrium distribution in the interior of the field as the first guess. It is observed that about 50 iterations of the entire field are adequate to get a convergence level of less than 1 percent stipulated by (43).

IV. General survey of the investigations on the transport processes in the stratosphere

To make an investigation on the problem of seasonal variations of atmospheric ozone it is necessary to know about the large scale diffusive and advective phenomena. Studies made on the transport processes in the atmosphere have in general a tendency to emphasize one of the two major transport phenomena: diffusion or advection. Theories constructed on the basis of either one of these two seem to be capable of explaining phenomena such as the spread of radioactive debris in the stratosphere. An attempt is made here to present an account of both of these schools of thought.

Brewer (1949), from his frost point hygrometer measurements of water vapor content in the lower stratosphere

over Great Britain, observed a rapid fall of humidity mixing ratio above the tropopause. The humidity mixing ratio at a height of 1 km above the tropopause was about one-tenth of its value at the tropopause. The frost points at 15 km were as low as the lowest temperatures measured in the upper troposphere near the equator. Thus he argued that such extremely dry air present in the polar stratosphere must have originated in the equatorial upper troposphere. Brewer explained the vertical distribution of water vapor in the lower polar stratosphere as a result of upward diffusion of water vapor opposed by a slow sinking of very dry air from above. A reverse current from the troposphere into the stratosphere in the equatorial region was postulated to balance such a slow sinking of air in the higher latitudes from the stratosphere into the troposphere.

Brewer estimated from the observed vertical profiles of water vapor distribution a value of 1.8×10^{-5} to $5 \times 10^{-5} cm^{-1}$ for the ratio w/K_z, where w(cm/sec) is the velocity of the sinking motion, and $K_z (cm^2/sec)$ is the vertical eddy diffusion coefficient, in the lower stratosphere. He also suggested that the effect of horizontal advection could be only one-tenth of sinking. These ideas of Brewer were accepted by Dobson (1956) to explain the seasonal distribution of ozone in the atmosphere. The

circulation model thus came to be know as the "Dobson-Brewer" model.

The most important factor, namely the nature of the vertical distribution of water vapor in the stratosphere, which led Brewer to postulate his model of the organized circulation in the stratosphere, does not appear to be a general characteristic of the stratosphere on the whole globe. The water vapor mixing ratio is observed sometimes to increase with height in the stratosphere (Mastenbrook et al., 1961).

Murgatroyd and Singleton (1961), neglecting the influence of large scale diffusion, have made a calculation of meridional circulation sufficient to transport heat between radiational sources and sinks in the stratosphere (15-55 km) and mesosphere (55-80 km). Combining suitably the radiative heating values of Ohring (1958) and Murgatroyd and Goody (1958), and modifying slightly the combined radiative field to get a solution, they computed the meridional circulation. The radiative heating and the atmospheric temperature needed as a function of time in their computations were obtained with an implicit assumption that these two quantities are in phase with the sun.

The circulation model thus obtained has a rising motion of air below 30 km over the tropical latitudes, with

an outflow from the tropics to higher latitudes in both hemispheres. The order of magnitude of the vertical velocity is 10^{-1} cm/sec, and below 40 km the horizontal velocity is about 10^{2} cm/sec.

Cross-sections of meridional and vertical velocities from pole to pole at different times of the year computed by Murgatroyd and Singleton (1961) are presented in the Fig. 11.*

Broadly speaking, the circulation model of Murgatroyd and Singleton suggests rising motion in the tropical latitudes somewhat following the sun in its transit from one hemisphere to the other during the year. In the summer hemisphere at higher latitudes most of the stratosphere is covered with rising motion, and in the winter hemisphere there is correspondingly an intense sinking motion. The circulation model for autumn and spring shows an appreciable difference between the circulation on either side of the equator, with relatively intense mean air motions in spring and weak circulation in autumn. The poleward velocity in general in all seasons intensifies as one goes to lower levels in the stratosphere.

This circulation model of Murgatroyd and Singleton supports the ideas of the "Dobson-Brewer" model. However, the authors remarked that systems on the scale of cyclones

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*Royal Meteorological Society Quarterly Journal, 1961, vol. 87, page 130; Fig. 2.

and anticyclones, and possibly also diffusion, must play a large part as transport processes in the atmosphere, and that the circulation model obtained by them can be no more than a resultant mean effect.

Spar (see Stebbins, 1960), from his analysis of the spread of an artificial radioactive nuclide, W^{185} (Tungsten 185), introduced by the U. S. Hardtack nuclear explosions in 1958, derived meridional and vertical eddy diffusion coefficients for the stratosphere. Assuming that the radioactive cloud has a normal distribution of debris about the maximum, he obtained h, the half width of the cloud, as $h = 1.67\sqrt{Kt}$, where K (cm^2/sec) is the eddy diffusion coefficient and t is the time elapsed after detonation. He thus estimated that the value of the vertical eddy diffusion coefficient was 2×10^4 cm^2/sec at the polar latitudes and $4 \times 10^6 cm^2$/sec at the equatorial latitudes. The estimates of the meridional eddy diffusion coefficient ranged from a low value of about $5 \times 10^6 cm^2$/sec to a value almost as high as $10^{10} cm^2$/sec. However, the latitudinal variation of the meridional eddy diffusion coefficient could not be ascertained from this investigation.

W^{185} was observed to have a zone of maximum concentration around 65,000 - 70,000 ft. at the equatorial stratosphere and sloped down toward the poles. Furthermore, the height

of the zone of maximum concentration was found to be virtually stationary from September, 1958, to April, 1960 (Feely and Spar, 1960), contradicting the "Dobson-Brewer" calculation model, which hypothesizes an organized meridional circulation with air moving upward through the equatorial tropopause, then horizontally poleward at high levels, and sinking back into the troposphere in the polar region.

Feely and Spar (1960), to explain such an observed distribution of W^{185}, hypothesized a mixing mechanism in which lateral mixing occurs within a sloping layer which decreases in height toward the poles. However, they pointed out "the fact that the mixing surfaces slope more steeply than the isentropic surfaces may indicate the existence of a systematic sinking of the radioactive debris relative to the air as it mixes poleward, possibly by gravitational settling or some other mechanism, or a systematic subsidence of air itself as it mixes into the polar region. There is no indication, however, of a large scale subsidence of polar stratospheric air from very high levels."

Considering the rate at which the half width of the W^{185} cloud, in the north-south direction, increases with time, Spar (see Friend, et al., 1961) has deduced an effective meridional (poleward) velocity of 8 cm/sec which he states is about one fifth that of Murgatroyd and Singleton's

value. Further to account for the inclination, 1:1000, of the zone of W^{185} maximum from equator to pole, he has shown that there should be a rising motion of about 0.01 cm/sec at the equatorial region and a sinking motion of the same magnitude at the higher latitudes. This is about one tenth of the vertical velocity of Murgatroyd and Singleton in the lower stratosphere. Thus the terminal velocity of the tungsten-bearing particles, which are apparently held stationary in the rising motion at the equatorial region, must be 0.01 cm/sec. From Stoke's law, one would find the radii of these particles to be about 0.2 microns, which Spar mentions is in good agreement with the size of the observed particles.

Murgatroyd and Singleton conclude from their trajectory calculation that "most of the air in the stratosphere, up to 25 km at least, must have passed through the equatorial tropopause region within the last one year or so." Commenting on this statement, Spar (see Friend, et al., 1961) points out that if this were so the radioactive debris from nuclear tests would be almost depleted in one year or so. Such a rapid depletion of radioactive debris, however, does not seem to get support from the observed amount of debris contained in the stratosphere.

An interesting feature concerning the meander of the

the center of W^{185} maximum about the equator was revealed from the investigations of Friend, et al., (1961). The W^{185} maximum, although held to a stationary height, was found to migrate to the southern hemisphere during winter, and by early summer was back in the northern hemisphere. This phenomenon suggests a tendency of the peak of the W^{185} cloud to follow the sun.

Spar (see Friend, et al., 1961) indicated that direct vertical mixing through the tropopause appeared to be too small to account for the stratospheric fallout.

A recent survey by Newell (1961) is very helpful in assessing the relative importance of large scale diffusion processes and mean meridional motions in the stratosphere. Newell has estimated the horizontal eddy transport of ozone by an elegant and simple method. Assuming that the ozone concentration in the layer 12-24 km is correlated with total ozone measured at the ground he has evaluated the large scale meridional horizontal eddy flux of ozone from the winds in that layer. This computation was based on data obtained during the I.G.Y. from twenty-five ozone stations that had local upper air wind observations. He has also estimated the meridional transport of ozone due to mean meridional motion. Newell's investigations suggest that the transport due to large scale horizontal eddies is in general very large compared to the transport due to mean

meridional motion. For instance, the values of the eddy transport and the transport due to mean motion at 50°N during spring 1958, according to him, are in the proportion 11.0:1.8. Both these transports of ozone are directed toward the north. Newell further demonstrates quantitatively that these transports are capable of accounting for the observed build-up of ozone at higher latitudes during winter and spring.

V. Discussion of the results

A. Computed models of the meridional distribution of ozone.

The photochemical equilibrium distributions of ozone calculated for the solstices and the equinoxes are presented in Fig. 12 and 13. Both these distributions indicate a center of ozone high located at about 30 km height at the latitude over which the sun is overhead. The concentration of ozone decreases in all directions from this center. A clear symmetry of the ozone distribution about the vertical at the latitude over which the sun is overhead may be noticed.

A comparison of the photochemical equilibrium distributions of ozone shown in Figures 12 and 13 with those of the "observed" models in Figures 1 and 2 reveals all the inadequacies of the pure photochemical theory. Further, we are led to infer from such a comparison, the important part played by transport mechanisms present in the atmosphere.

From the earlier discussion in Section IV on the transport processes--namely, large scale diffusion and mean meridional motions--it is not easy to arrive at a comprehensive unified picture of these transport processes. A computation of such a unified model of the transport processes that includes both diffusion and mean meridional motions is beyond the scope of this work. Instead, an attempt is made in this study to combine the mean meridional motions depicted by Murgatroyd and Singleton and the diffusion model of Spar with the help of investigations made by Newell in which an evaluation of the relative importance of each one of these transport processes is made.

The large scale diffusion model of Spar for the stratosphere suggests that the vertical eddy diffusion coefficient increases from a low value of $4 \times 10^3 cm^2/sec$ in the tropics to $2 \times 10^4 cm^2/sec$ at the polar latitudes. The variation of the horizontal eddy diffusion coefficient with latitude could not be so readily ascertained. Hence the variation of the horizontal eddy diffusion coefficient has to be elicited from an experimentation with the calculations on the model of the meridional distribution of ozone.

The experimentation on the meridional distribution of ozone under steady state condition for the equinoxes is first undertaken.

From a few trial calculations with a constant value of 2×10^9 cm^2/sec for the horizontal eddy diffusion coefficient, a rapid increase in the value of K_z, the vertical eddy diffusion coefficient from tropical latitudes to the polar latitudes as shown in Table 1, is chosen.

Table 1. Variation of K_z with latitude for the equinoxes.

Lat°	0	10	20	30	40	50	60	70	80	90
K_z $10^4 \cdot cm^2/sec$	0.4	0.4	0.6	0.9	1.4	2	2	2	2	2

From similar experimentation an optimum value of about 20 percent of the Murgatroyd and Singleton circulation (comprising the meridional and vertical velocities) for the equinoxes is arrived at. Apparently this estimate of the mean meridional circulation, in a broad sense, is in agreement with the estimate of the mean meridional motion arrived at by Friend, et al., (1961) from their investigation on the rate at which the half width of the W^{185} cloud increased in the north-south direction. Newell's (1961) estimate of the mean meridional motion also seems to support this evaluation of the Murgatroyd and Singleton mean meridional circulation.

The model of the distribution of ozone calculated

for the equinoxes as explained in III-B, with the above scheme of transport processes, is shown in Fig. 14.

The concentration of ozone on the tropopause, the lower boundary of the model, is specified with the help of the "observed" distribution of Paetzold, et al., (Fig. 4) for spring and autumn.

The computed model thus obtained for the equinoxes still shows the ozone high produced by solar radiation over the tropical latitudes. However, there is a reasonably good lateral spread of ozone that is best illustrated in Fig. 15B in which the latitudinal variation of total ozone calculated for the equinoxes is plotted. The total ozone obtained from the photochemical equilibrium calculation for equinoxes is shown in Fig. 15A for comparison.

From the scheme of the transport processes used to calculate this (Fig. 14) distribution of ozone, it is obvious that the diffusion pattern is symmetrical about the equator. There is, however, asymmetry of circulation present between the spring and autumn hemispheres. Such superficial argument cannot be carried further to conclude that the difference between the distribution of ozone between spring and autumn is due entirely to the difference in circulation intensity. Such a conclusion is misleading. The large scale diffusion processes in the vertical and horizontal

directions interact in a nonlinear fashion with the mean meridional circulation. It is more justified to infer that the difference between the latitudinal distribution of ozone in spring and autumn is a result of the mutual interaction of the circulation and diffusion phenomena.

The increase of total ozone with latitude shown in Fig. 15B is inadequate to explain the total ozone increase with latitude portrayed by London (1962) for spring and autumn. This immediately leads one to an examination of the horizontal eddy diffusion coefficient. Spar's investigations show that the horizontal eddy diffusion coeffidient has a large range of values. Therefore further experimentation on the meridional distribution of ozone has been done, increasing the horizontal eddy diffusion coefficient from tropical latitudes to polar latitudes. Eventually a variation of K_Y somewhat analogous to the variation of K_Z with latitude has been found suitable. The variation of K_Y thus arrived at is shown in Table 2.

Table 2. Variation of K_Y with latitude for the equinoxes.

Lat^o	0	10	20	30	40	50	60	70	80	90
K_Y $10^{10}\cdot cm^2/sec$	0.2	0.2	0.4	0.6	0.8	1.0	1.0	1.0	1.0	1.0

The meridional distribution of ozone, calculated with such a variation of K_y along with the model of the K_z and mean meridional motion used in the preceding computation, is shown in Fig. 16. The variation of the total ozone with latitude given by this distribution is plotted in Fig. 17.

The increase of total ozone from tropical latitudes to the polar latitudes shown in Fig. 17 is in better agreement with that of London's curves for spring and autumn. On the basis of reasonable agreement between the observed total ozone curves and the computed ones, it is felt that, in order to explain the spring build-up of ozone at higher latitudes by the steady state approach, increase of the horizontal eddy diffusion coefficient from tropical latitudes to polar latitudes is necessary.

After having studied in detail the behavior of the various transporting mechanisms for the spring and autumn seasons, it is straightforward to proceed to the summer and winter seasons. Furthermore, the quantitative model of the transport mechanisms developed to explain the distribution of ozone for spring and autumn may now be checked in the computation of the steady state distribution of ozone for summer and winter.

From the observations made by Friend, et al., (1961) on the W^{185} cloud it is apparent that the center of the cloud has a tendency to move with the sun. This interest-

ing detail suggests a shift of the whole pattern of the diffusion field along with the sun. In other words, the hemisphere tilted toward the sun has a comparatively weak pattern of diffusion, while the hemisphere tilted away from the sun has a correspondingly more intense mixing. Such an idea seems to be quite consistent with the relatively stable lapse rates of temperature in the summer stratosphere and comparatively less stable lapse rates and polar night jet stream (Hare, 1960) in the winter stratosphere.

The above ideas have been suitably used to adjust the diffusion pattern for the summer and winter hemispheres as shown in Table 3.

Table 3. Variation of K_z and K_y with latitude for the solstices.

Summer

Lat^{o}	10	20	30	40	50	60	70	80	90
$K_z \cdot 10^4$ cm^2/sec	0.4	0.4	0.4	0.6	0.9	1.4	2.0	2.0	2.0
$K_y \cdot 10^{10}$ cm^2/sec	0.2	0.2	0.2	0.4	0.6	0.8	1.0	1.0	1.0

Winter

Lat^{o}	0	10	20	30	40	50	60	70	80	90
$K_z \cdot 10^4$ cm^2/sec	0.6	0.9	1.4	2.0	2.0	2.0	2.0	2.0	2.0	2.0
$K_y \cdot 10^{10}$ cm^2/sec	0.4	0.6	0.8	1.0	1.0	1.0	1.0	1.0	1.0	1.0

With the pattern of vertical and horizontal eddy diffusion shown in Table 3, and with 20 percent of Murgatroyd and Singleton's mean meridional circulation for the solstices, a steady state distribution of ozone is calculated as explained in III-B.

The boundary condition on the tropopause is again specified from the Paetzold et al., model. It is tacitly assumed here that the concentration of ozone on the tropopause in winter is similar to that in spring, and in summer is similar to that in autumn. Such as assumption may not be unreasonable if one considers the latitudinal distribution of total ozone during these seasons. Incidentally, this assumption provides a good ground to test the influence of the lower boundary condition on the distribution of ozone in the interior of the field of computation.

The distribution of ozone resulting under steady state condition for solstices calculated with the above boundary condition on the tropopause is shown in Fig. 18. The variation of total ozone with latitude computed for the corresponding seasons is plotted in Fig. 18.

The latitudinal increase of total ozone for winter and summer shown in Fig. 18 reveals some significant departures from the corresponding curves of London (1962). The solar radiation incident normally at 23.5° latitude on the summer

hemisphere in the computed model has apparently contributed to comparatively larger values of the total ozone in the tropical latitudes. In the winter hemisphere the total ozone from the computed model in the tropical latitudes seems to be appreciably smaller than that given by London's curve. The relatively larger total amounts of ozone in summer and smaller amounts in winter in the tropical latitudes shown by London's curves, lends a qualitative support to the computed results. London's curves show a maximum difference of about 30 D.U. between the summer and winter at the equator with a mean total ozone of about 250 D.U. The computed total ozone curves show a maximum difference of about 48 D.U. at about 25° latitude with a mean total ozone of about 258 D.U.

Although the total ozone variation with latitude computed for the four seasons shown in Fig. 17 qualitatively agrees with the observed curves (London's), there is considerable disagreement between the two. The total ozone computed for spring and winter is still short of the observed increase of ozone for those seasons. On the other hand, the calculated total ozone for summer and autumn is considerably larger than that suggested by the observed values. The difference between the winter and summer total ozone from the observed values, at higher latitudes, is almost double that obtained from the computations.

The seasonal variation of ozone in this study is computed with an assumption of steady state conditions. Such an assumption may not be justified for each season, but should be valid for the mean annual ozone distribution with latitude. The mean annual total ozone distribution is obtained from the computed total ozone curves for the four seasons as shown in Fig. 19. The mean annual total ozone distribution constructed in this fashion is in reasonable agreement with that of the observed total ozone curves (London 1962).

Until now the discussion on the computed meridional distributions of ozone has been based on the total ozone variation with latitude. The emphasis laid on the total ozone rather than the details of its distribution in the meridional plane is mainly due to the fact that the total ozone is the only parameter of atmospheric ozone known with a good degree of accuracy.

In general, all of the computed models of the meridional distribution of ozone do not quite resemble the "observed" models. Each one of the computed models clearly shows three ozone highs. One of these ozone highs is evidently produced by the solar radiation and is in the tropical stratosphere centered around 30 km height. The other two ozone highs are a result of the transport processes,

and their centers are located around 18 km height at the poles in spring, autumn and winter hemispheres. This center is around 20 km height at the summer pole.

The "observed" models of the meridional distribution of ozone do not indicate the existence of an ozone high in the tropical stratosphere. The ozone high close to the pole is present only in the model of Paetzold in the spring hemisphere.

In the computed models at higher latitudes, large horizontal and vertical gradients of ozone are present close to the tropopause during spring, autumn, and winter, while during summer a rather weak gradient is developed. The distribution of ozone in the lower stratosphere during summer is thus considerably different from the other three seasons. This is primarily a consequence of the weak diffusion pattern and the rising air motions present over large portions of the stratosphere in the summer hemisphere.

The "observed" models suggest the presence of strong horizontal and vertical gradients of ozone in the lower stratosphere at high latitudes during spring and probably during late winter.

The zone of ozone maximum, formed by the three ozone highs in both the equinoctial and the solsticial models of the steady state distribution of ozone calculated in this study, slopes down steeply from the subsolar point to the

poles. The "observed" models apparently do not indicate such a steep slope for the zone of ozone maximum.

From the above brief discussion of the meridional distribution of ozone, it may be remarked that the computed models differ from the "observed" models in many details, but the general patterns in both the computed and the "observed" models are similar. Until our knowledge of the "observed" distribution of ozone in the atmosphere is better than it is at present, it will not be possible to judge quantitatively the details of the computed models.

To test the influence of the lower boundary condition on the computed distribution of ozone in the interior of the field, a calculation of the ozone distribution for the solstices is made with radically different boundary condition on the tropopause. In the computed distribution shown in Fig. 18 the lower boundary condition has been taken to be exactly the same as that used for spring and autumn. Now in order to test the significance of the lower boundary condition, the distribution of ozone on the tropopause for winter is taken to be half that of spring, and for summer, twice that of autumn. Such an alteration of the boundary condition, however, is done from 40° latitude to the pole on either hemisphere as shown in Table 4.

Table 4. Modified value of the ozone concentration (10^{12} molecules/cm^3) at the tropopause in winter and summer.

Lat°	0	10	20	30	40	50	60	70	80	90
Winter	0.54	0.54	0.67	1.08	1.41	1.34	1.48	1.75	2.00	2.00
Summer	0.54	0.54	0.54	0.54	0.08	1.08	2.16	2.64	3.20	3.20

In order to bring to light the significance of the lower boundary condition, the total ozone variation with latitude corresponding to the two sets of lower boundary condition for solstices is presented in Fig. 20. Besides this, in Fig. 21 the vertical distribution of ozone, taken from the meridional distributions of ozone computed with these two different boundary conditions at 60° latitude in the winter and summer hemispheres, is presented.

From Fig. 21 it may be observed that changing the lower boundary condition does not affect the ozone distribution above about 20 km. The influence of the boundary value rapidly decreases with height. Changing the boundary value by a factor of 2 has altered the total ozone by about 8 percent. This comparatively small change is obviously due to the effect of the transport processes that strongly control the distribution of ozone within the interior of the field.

B. Limitations of the study

The study of the meridional distribution of ozone made in this investigation is purely a numerical experiment.

In this study the absorption coefficient of ozone in the spectral interval 2200 to 2020 Å is adopted, with suitable modification, from Vassy's (1941) photographic photometric measurements. If, however, the absorption coefficient of ozone, in the same spectral interval, reported by Tanaka et al., (1954) is used, one would get much larger photochemical production of ozone, especially at tropical latitudes. Then in order to reduce such large amounts of ozone produced at the tropical latitudes to the amounts observed, it is necessary to use rising motions in the tropical stratosphere of about the same magnitude as shown on Murgatroyd and Singleton's (1961) model. So the present study in which Vassy's absorption coefficient of ozone is used cannot unequivocally place the stratospheric meridional circulation at 20 percent of that of Murgatroyd and Singleton.

The calculation of the meridional distribution of ozone for different seasons has been made as though the mean seasonal transport processes and the mean solar insolation for the season tend to produce a quasi-stationary pattern

of ozone. Such an assumption can make the results obtained in this study not applicable in toto to the real atmosphere in which both the solar insolation and transport processes are varying with time. The seasonal variations of ozone computed in this study are especially subject to such a limitation. The mean annual total ozone distribution is probably the least affected quantity obtained in this investigation with the steady state assumption.

A more satisfactory study of atmospheric ozone would be that in which one does not have to invoke the quasi-stationary seasonal distribution of ozone. Such a study would call for an approach to this problem as an initial value problem. This implies that one should have a detailed and reliable initial distribution of ozone, and also good quantitative information on the seasonal variation of large scale transport processes in the atmosphere. In view of the lack of this detailed information demanded by the initial value problem, the present study has been made by taking a less satisfactory but more simple approach. Hence caution must be exercised in interpreting the results obtained from this study with a steady state assumption. The present investigation can be no more than a starting point to more sophisticated and realistic future studies of the atmospheric ozone. The satisfactory manner in which

the present investigation has accounted for the observed total ozone in the atmosphere can at best be only a crude but quantitative demonstration of the importance of the transport processes in distributing ozone in the atmosphere.

The models of the transport processes used in this investigation lack rigorous dynamical basis. The efforts made to synthesize the advective and diffusive fields in the atmosphere are purely from the point of view of explaining the seasonal variation of the atmospheric ozone. The ability of such a scheme of transport processes to explain the seasonal variation of temperature or W^{185} in the stratosphere is still questionable. The only justification that can be attributed to this scheme of transport processes is that it is within reasonable limits laid by the current theoretical and observational findings.

The variations of ozone in the east-west direction are by no means negligible. The investigations of the variation of total ozone by Bidner (1958) over Western Europe strongly suggest such zonal variations. The assumption of zonal symmetry of ozone made in this study is a very broad assumption.

The height of the tropopause is assumed to vary smoothly from tropical latitudes to higher latitudes. On the contrary, the observed shape of the tropopause shows

a discontinuity between the tropical and middle latitudes. Brewer (1960) and Friend, et al., (1961) have discussed at length the important part played by this break in the tropopause and the jet stream present at this break in the exchange of ozone and nuclear debris, respectively, between the troposphere and stratosphere. With the information available at present, it does not seem possible to introduce such features on a quantitative basis in this study.

The influence of the large scale fluctuating vertical velocities in the early spring, which produce explosive warming and a large rise of ozone (Godson 1960), has not been included in this study. Also the meridional transport due to the meandering waves and vertical motions associated with the jet stream present in the polar night (Hare 1960) has not been quantitatively incorporated.

VI. Summary and conclusions

In the light of the new data on solar radiation and other parameters necessary for photochemical calculations, a computation of the meridional distribution of photochemical equilibrium of ozone for solstices and equinoxes is made. It is found, in agreement with ideas of the earlier investigators, that the photochemical theory by itself cannot explain the latitudinal and seasonal variation of ozone.

To study the part played by transport processes in the stratosphere, the necessary equation which includes the combined effects of photochemical and transport processes has been developed for steady state conditions. With such an equation and using a scheme of transport process that is within reasonable agreement with the current ideas on transport processes in the stratosphere, meridional distribution of ozone produced under steady state conditions are calculated for equinoxes and solstices. The seasonal and latitudinal variation of total ozone thus obtained is in qualitative agreement with the observed variations of total ozone in the atmosphere shown by the investigations of London (1962).

Considering the limitations of this study, it is hard to say that all the problems concerning the behavior of ozone in the atmosphere have been answered quantitatively. But it may be remarked that the technique developed in this investigation is potentially good for studying the problem of atmospheric ozone. It is hoped that such a quasi-stationary approach would put the problem of ozone, at least as a first step, on a quantitatively understandable level.

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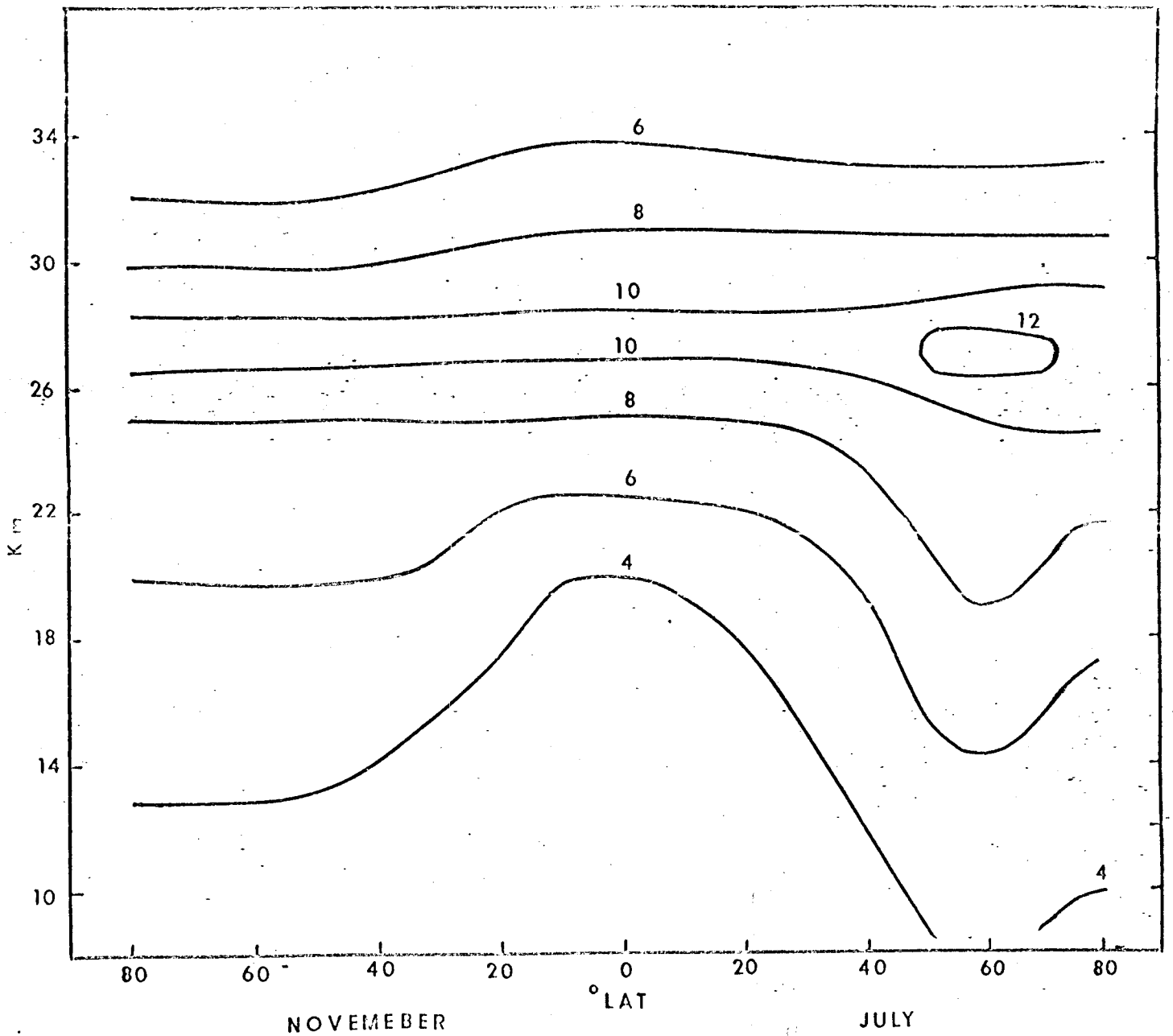

Fig. 1. Model of the "observed" meridional distribution of ozone (1.33 x D.U./km), constructed after Ramanathan and Kulkarni (1960).

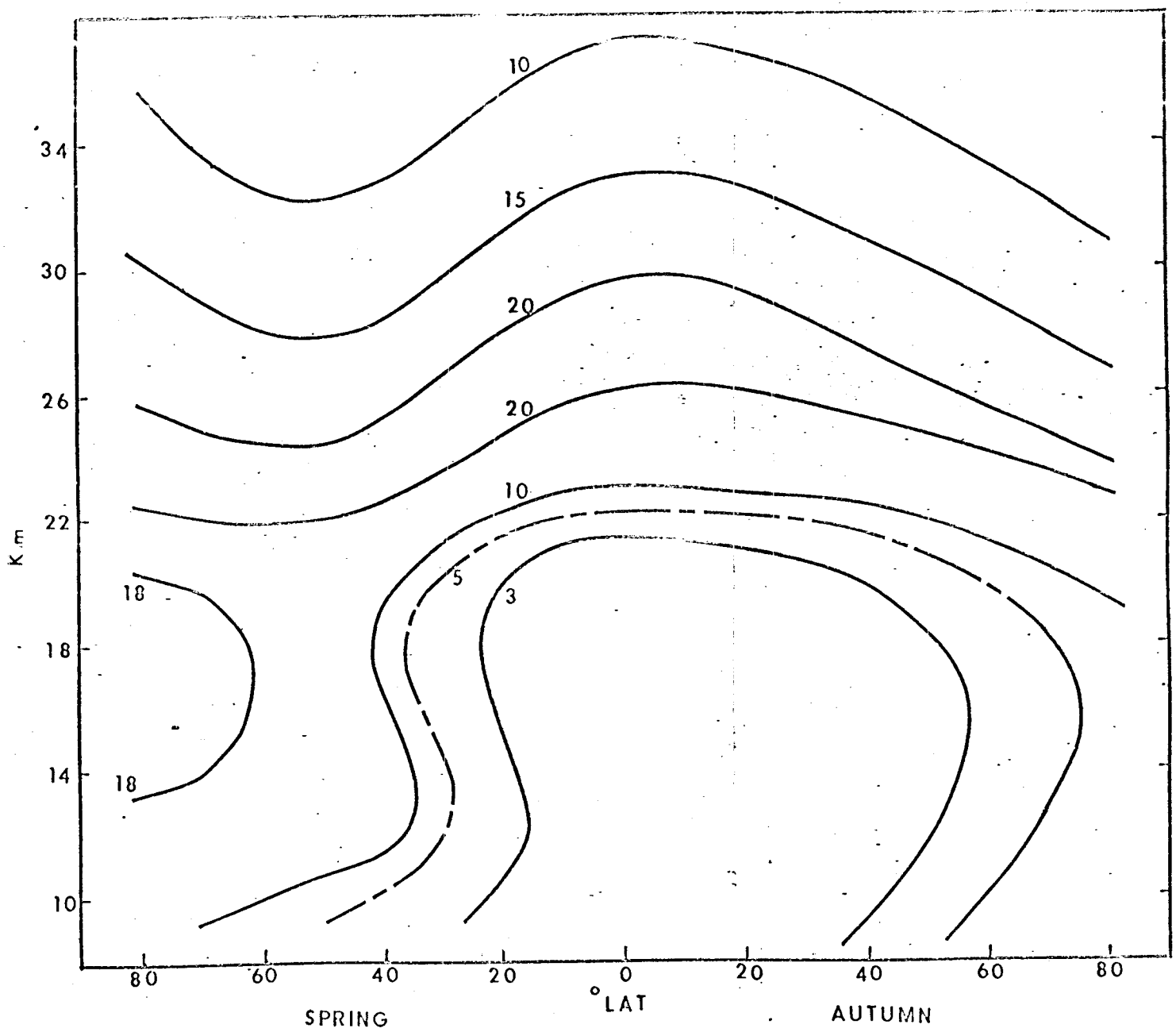

Fig. 2. Model of the "observed" meridional distribution of ozone (D.U./km) after Paetzold and Piscalar (1961).

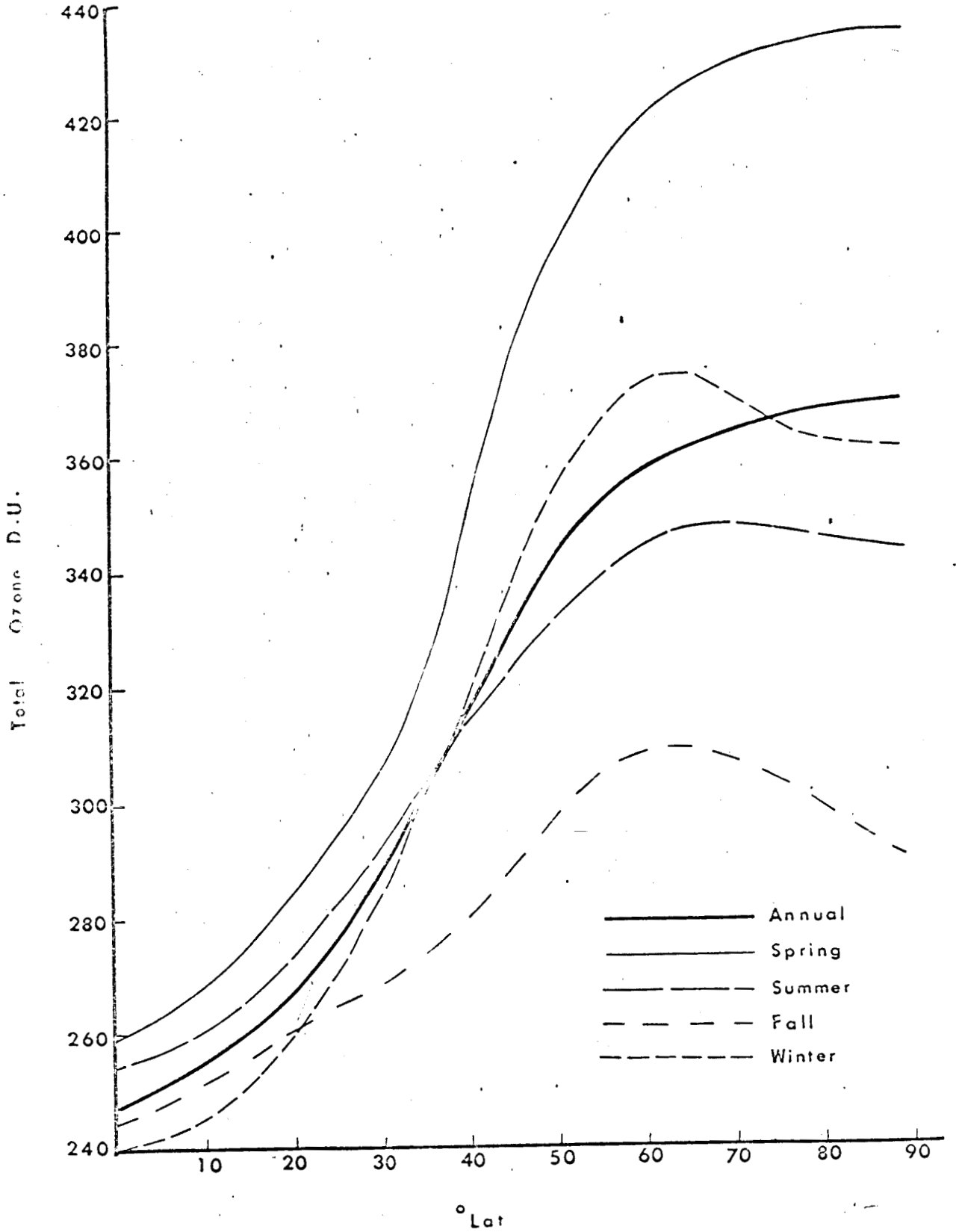

Fig. 3. Total ozone variation with latitude and season, after London (1962).

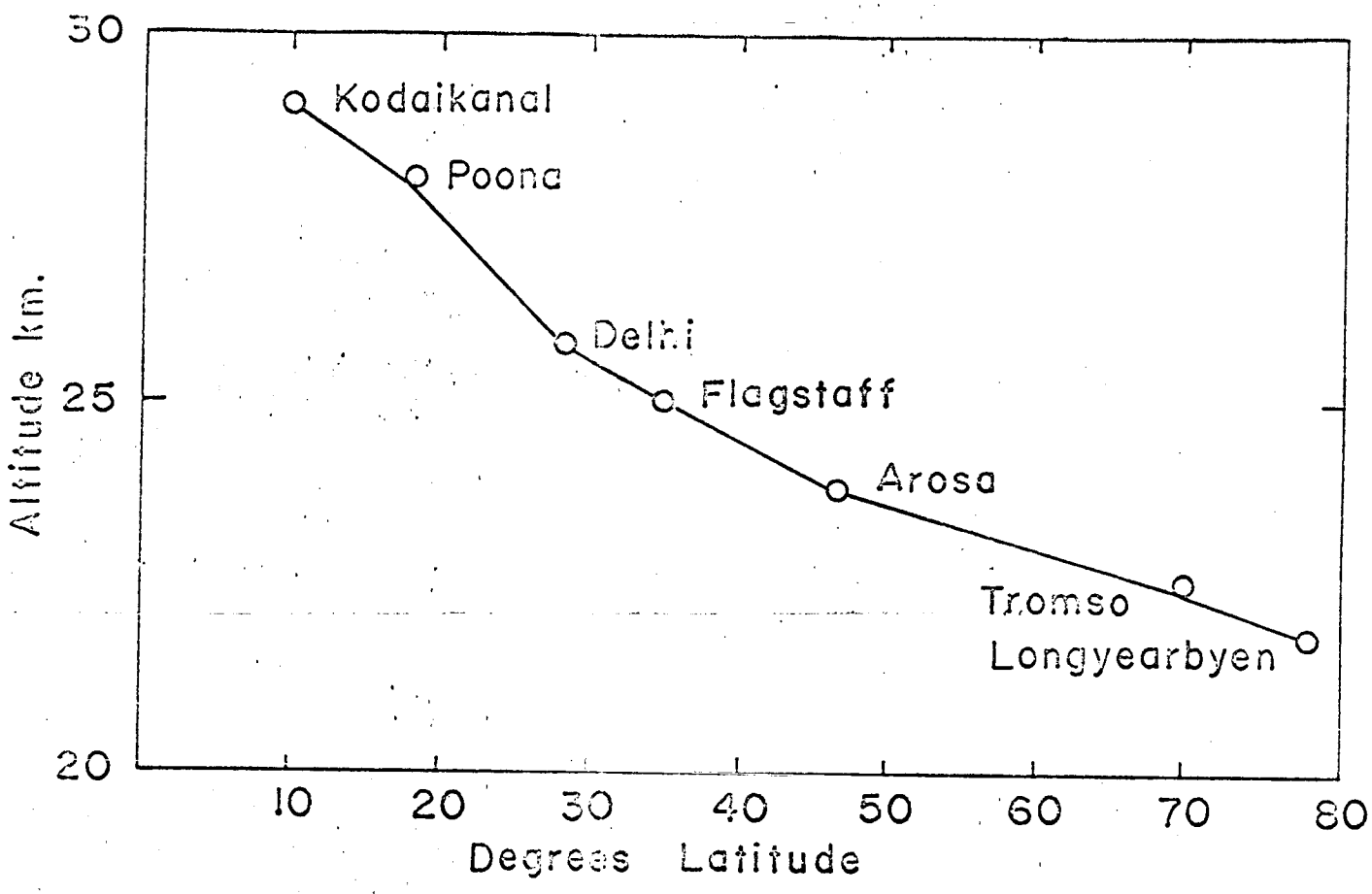

Fig. 4. Latitudinal variation of ozone center of gravity, after Miller (1960).

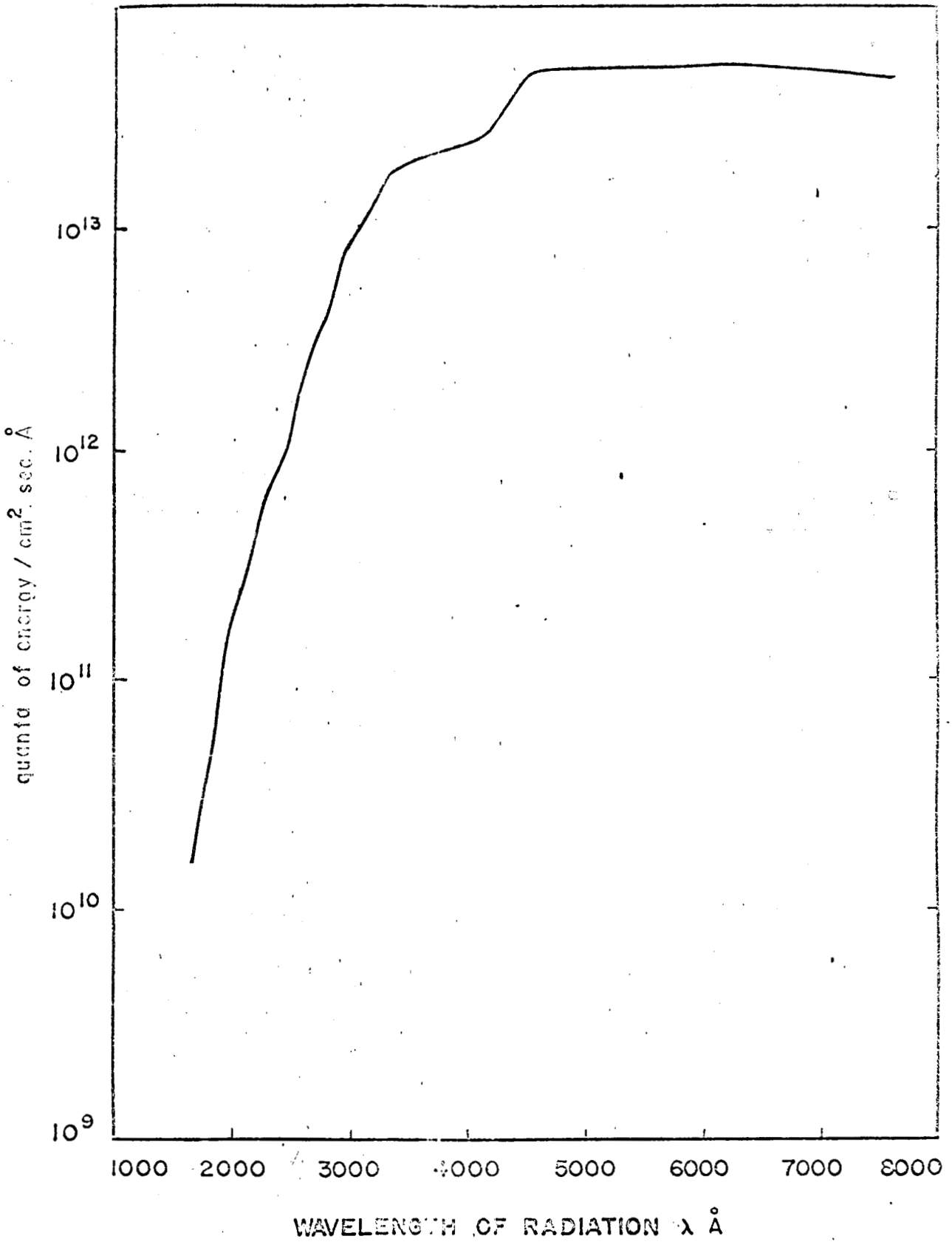

Fig. 5. Solar energy received at the top of the atmosphere.

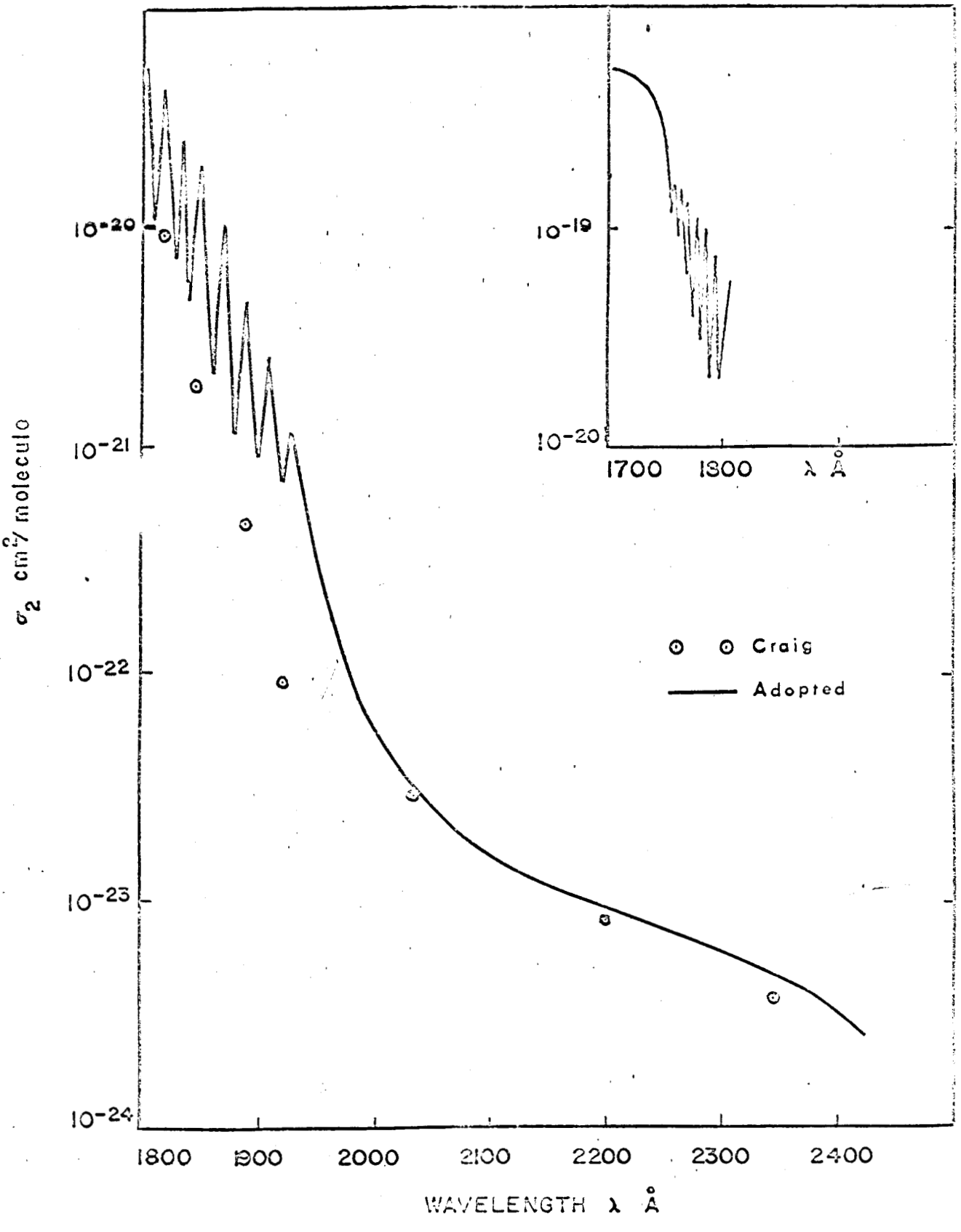

Fig. 6. Absorption coefficients of oxygen.

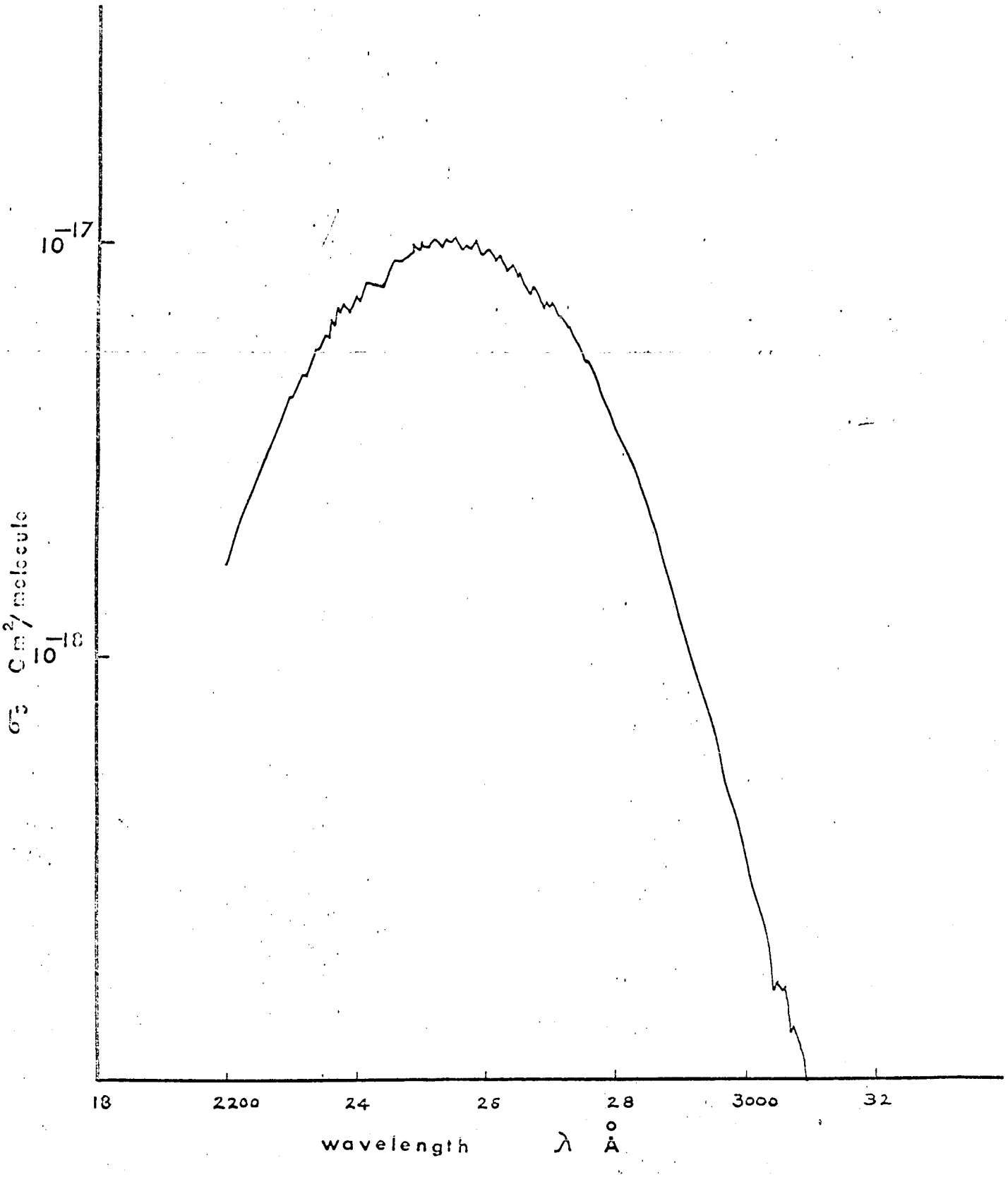

Fig. 7A. Absorption coefficients of ozone between 2200 and 3100Å.

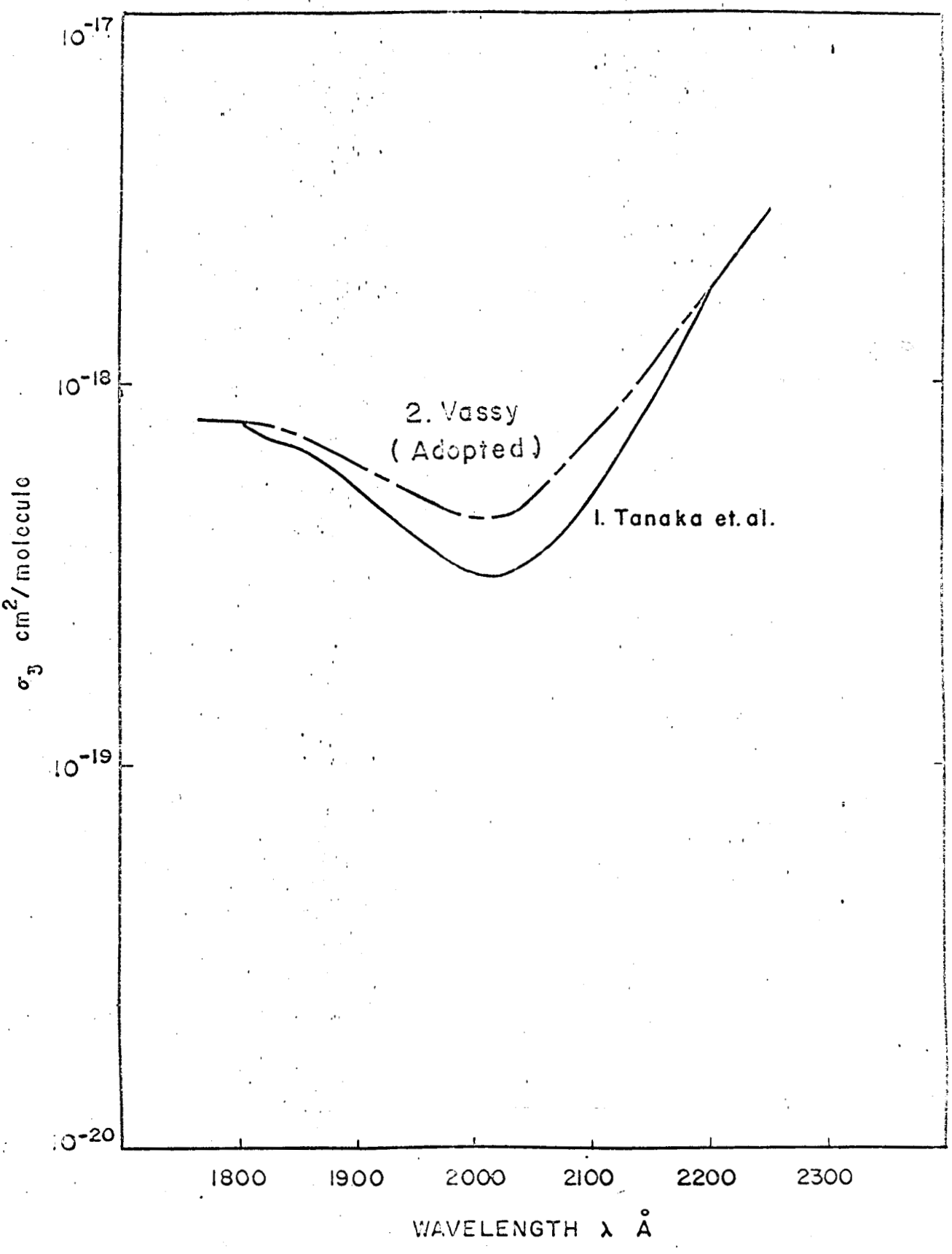

Fig. 7B. Absorption coefficients of ozone between 1800 and 2200Å.

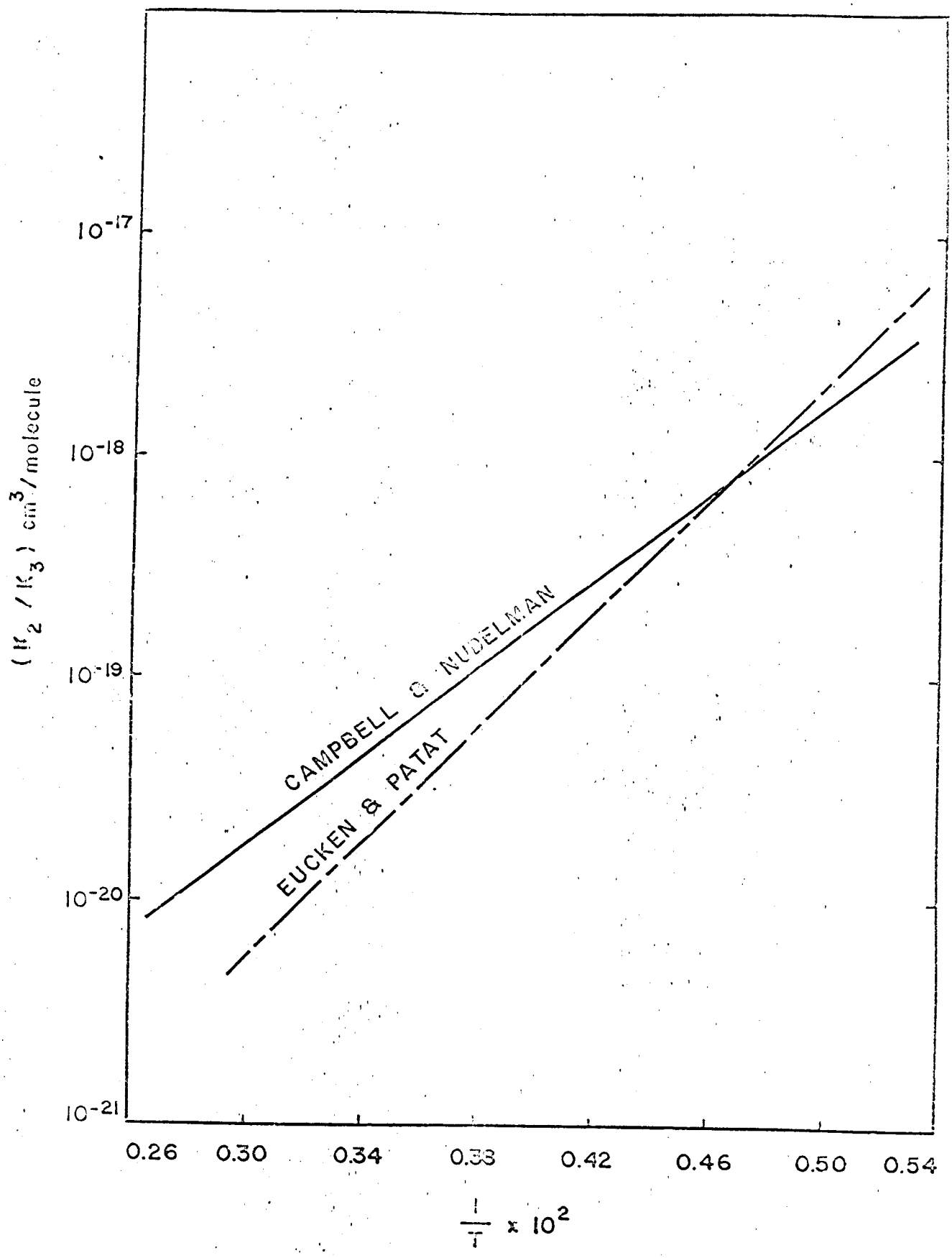

Fig. 8. Ratio of the reaction rate coefficients K_2 and K_3 vs $1/T°K$.

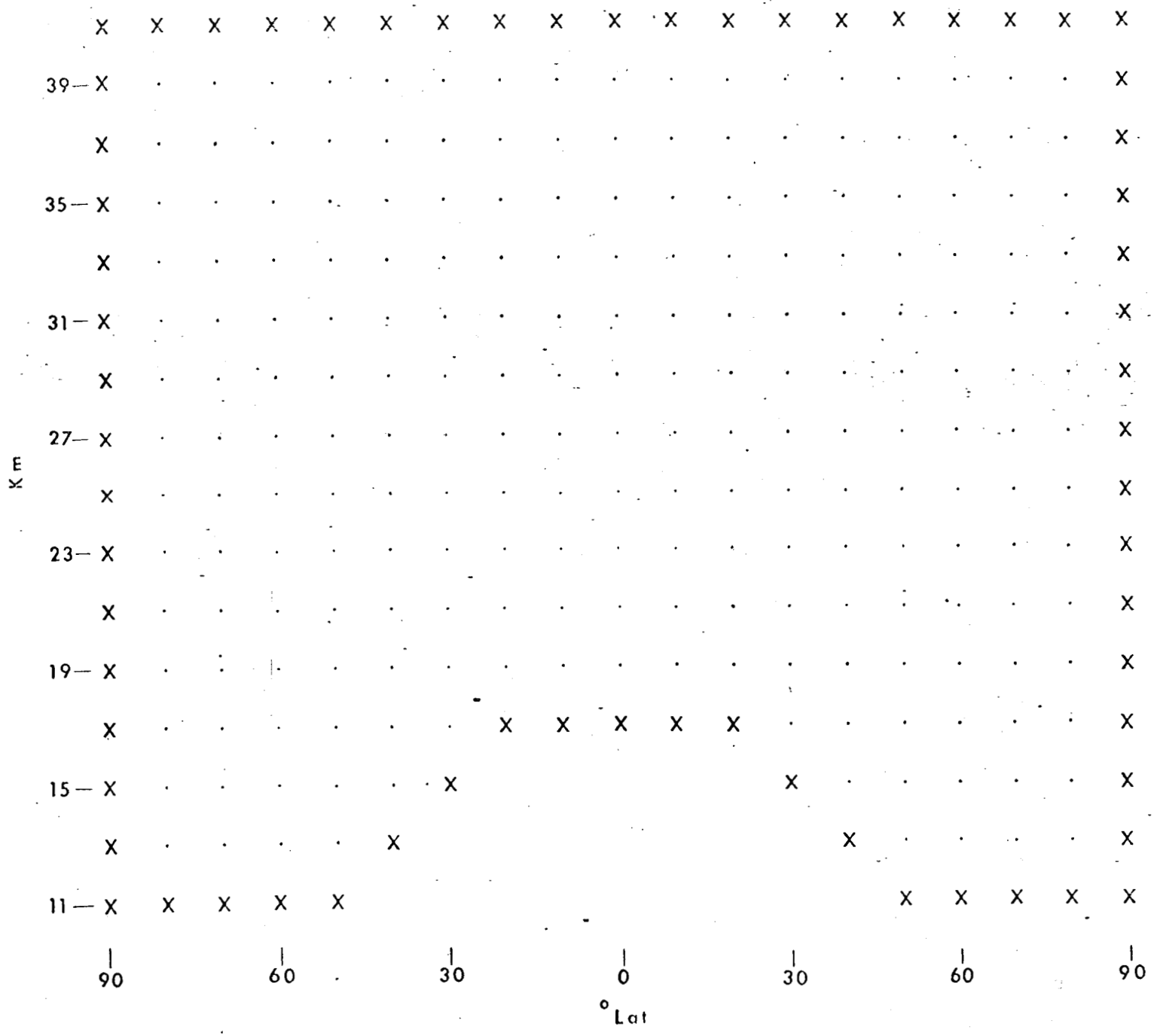

Fig. 9. Grid used for the numerical calculations.

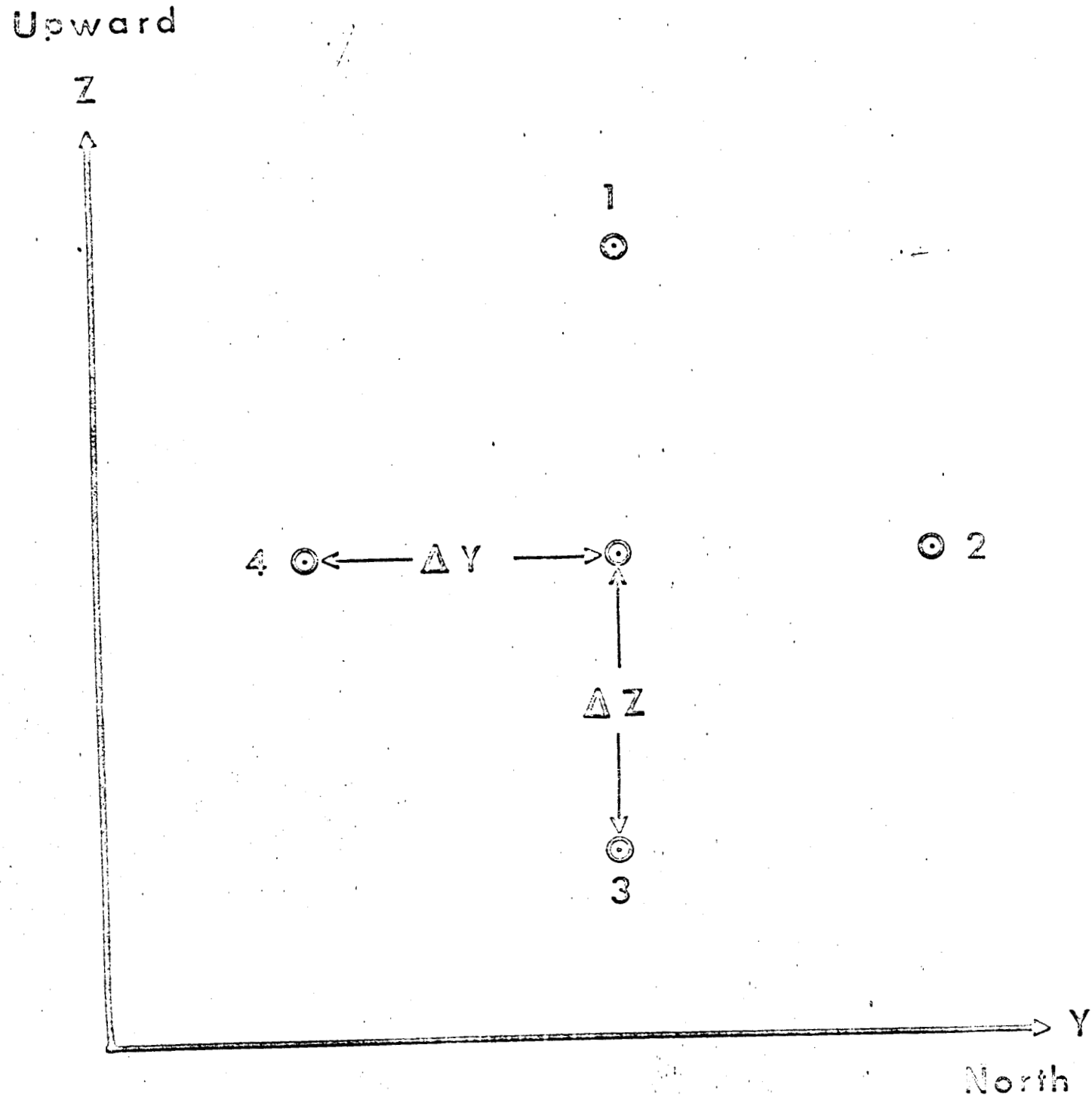

Fig. 10. Finite difference scheme.

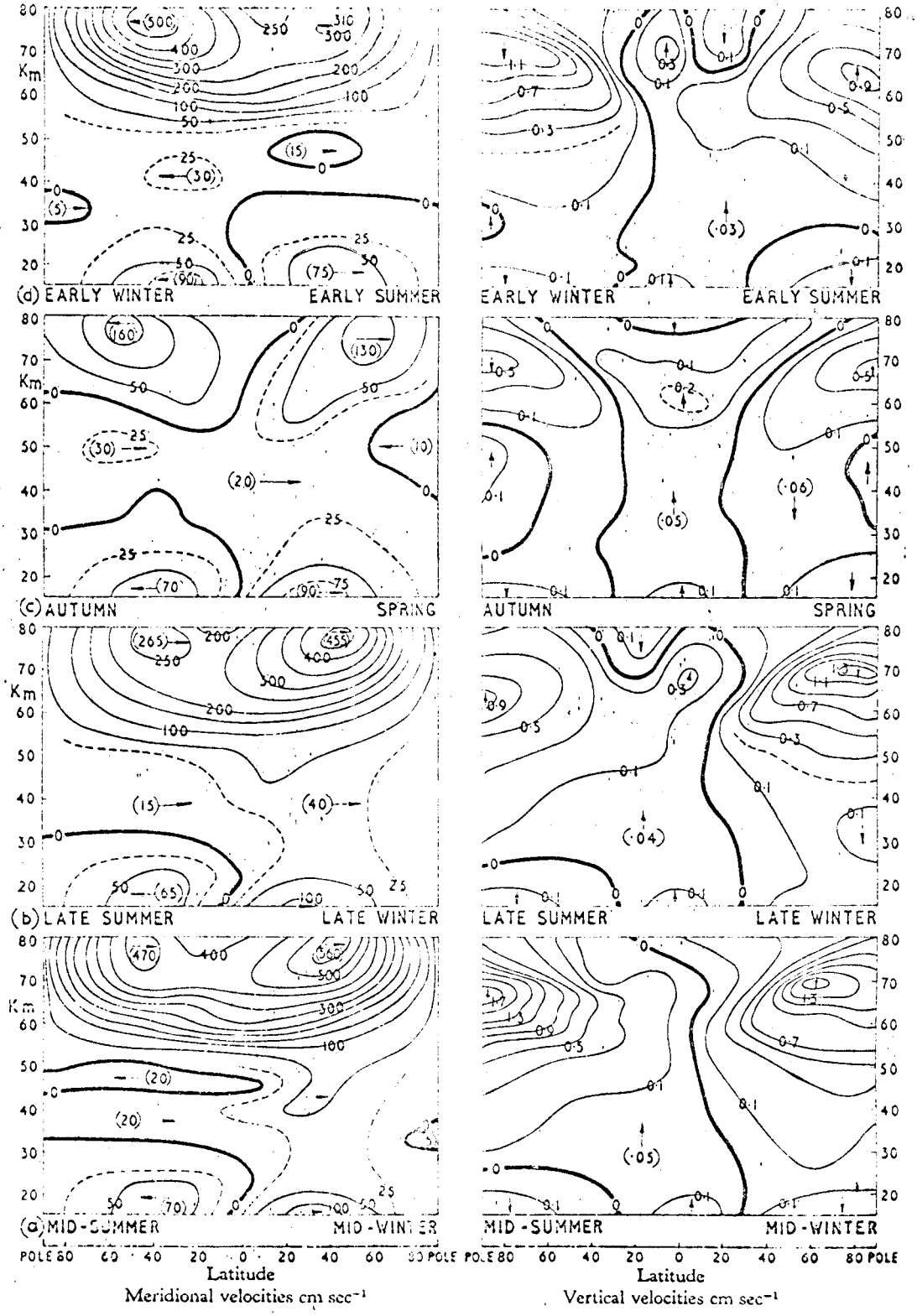

*Fig. 11. Cross-sections of meridional and vertical velocities (cm/sec^{-1}) from pole to pole at different times of the year (after Murgatroyd and Singleton, 1961). Courtesy of the Royal Meteorological Society Quarterly Journal.

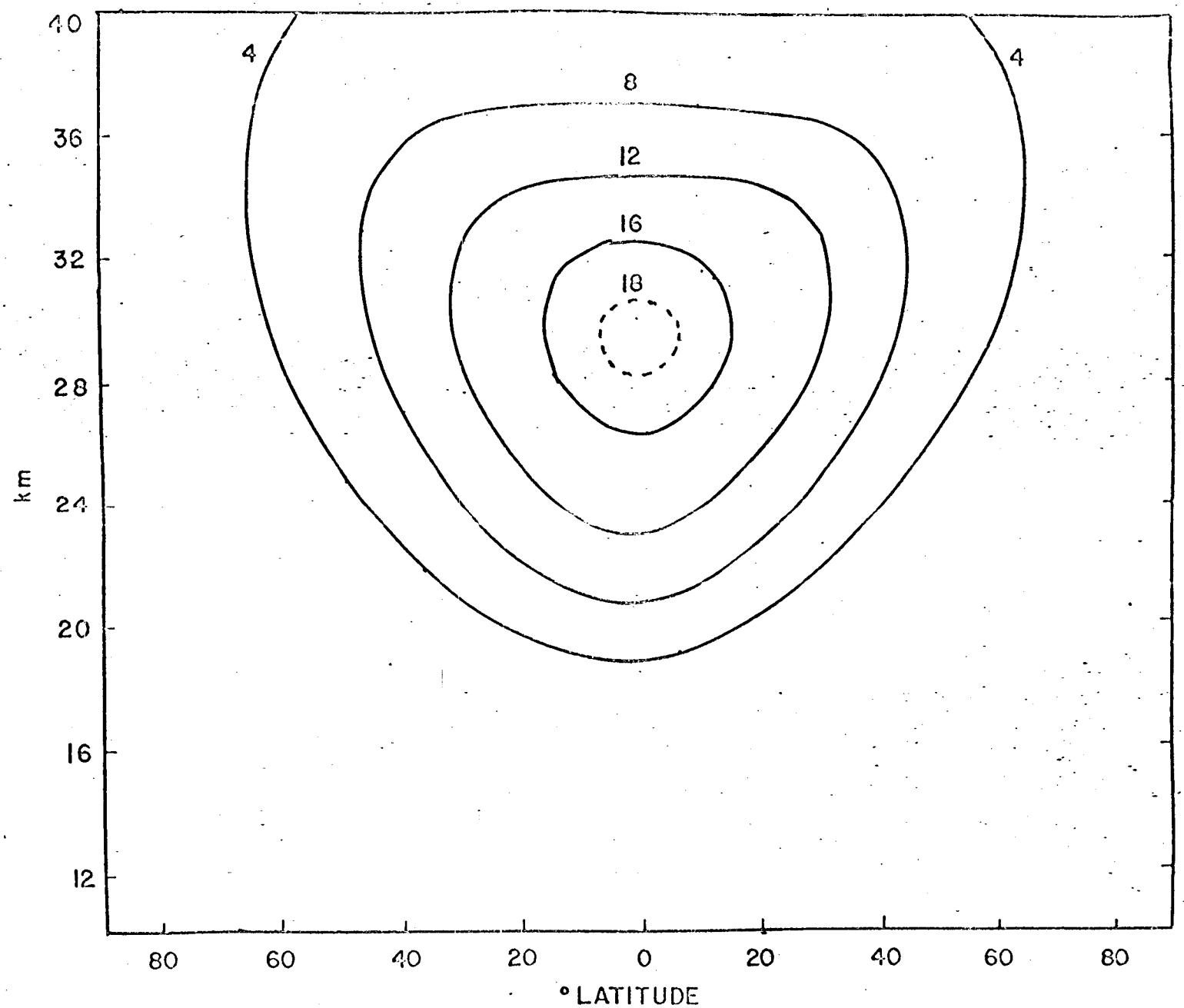

Fig. 12. Photochemical equilibrium distribution of ozone (D.U./km) for the equinoxes.

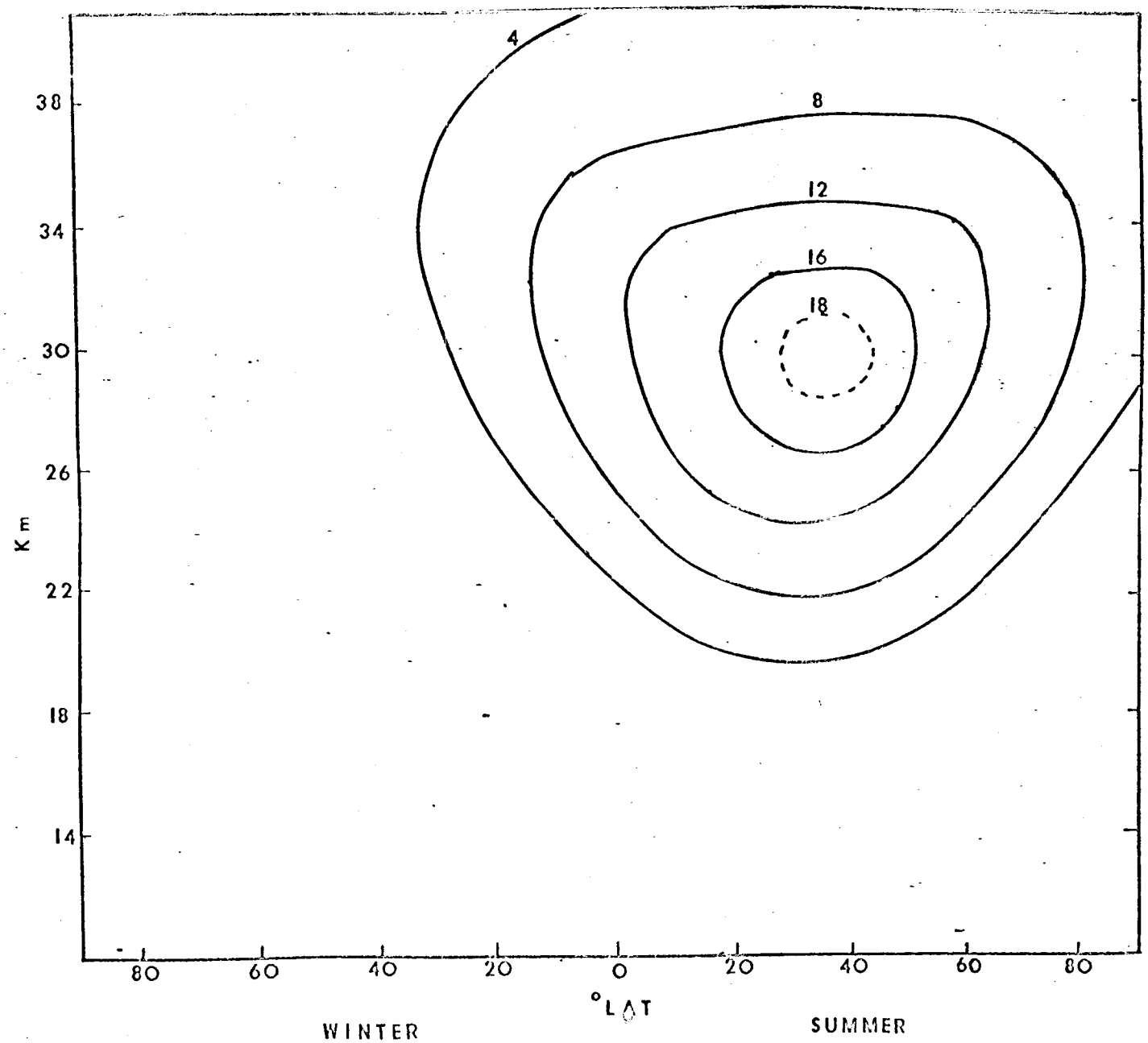

Fig. 13. Photochemical equilibrium distribution of ozone (D.U./km) for the solstices.

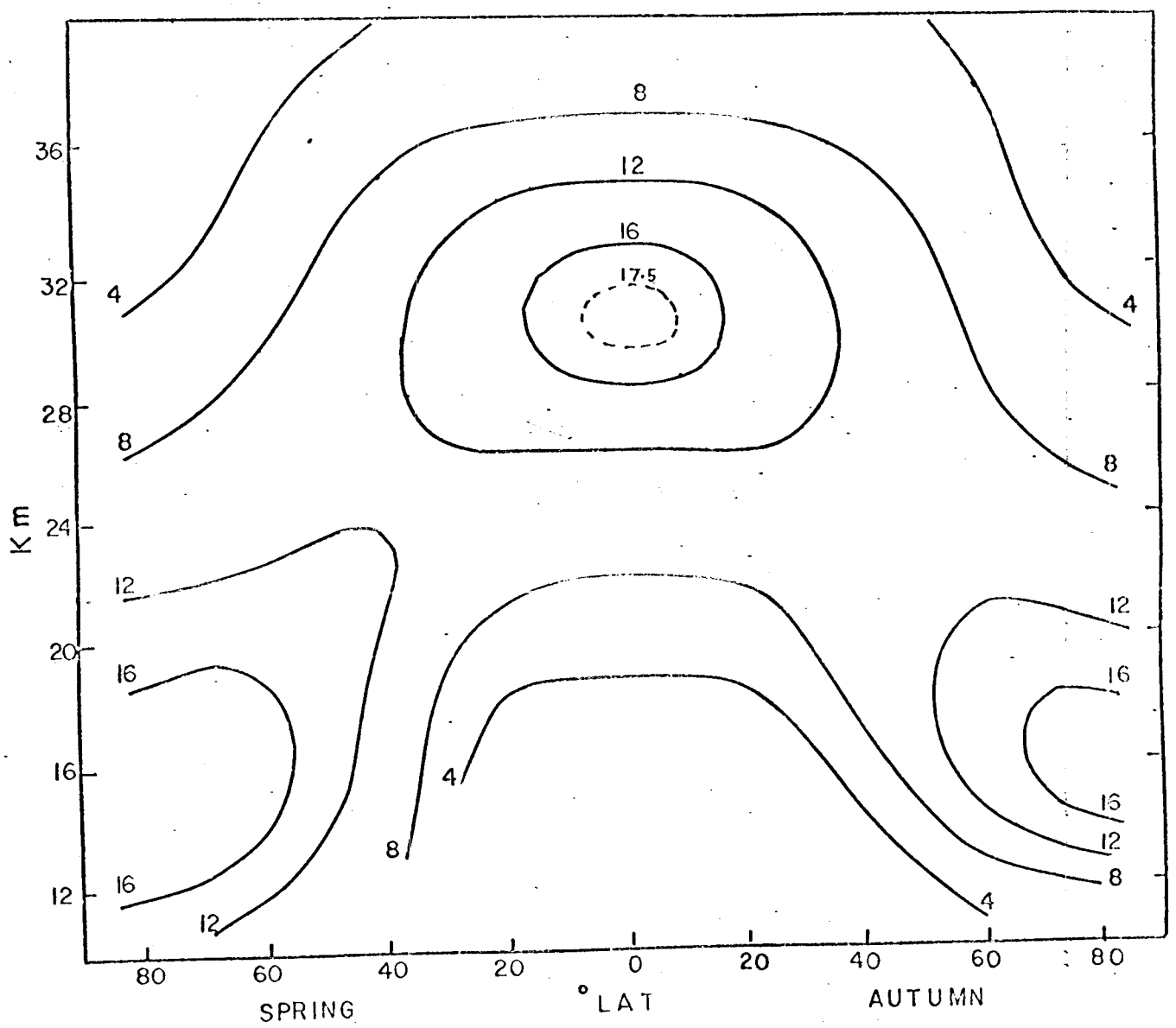

Fig. 14. Steady state distribution of ozone (D.U./km) computed for the equinoxes with constant value of K_y ($2 \times 10^9 cm^3/sec$), K_z (Table 1) increasing toward pole, and 20% of Murgatroyd and Singleton's (1961) mean meridional circulation.

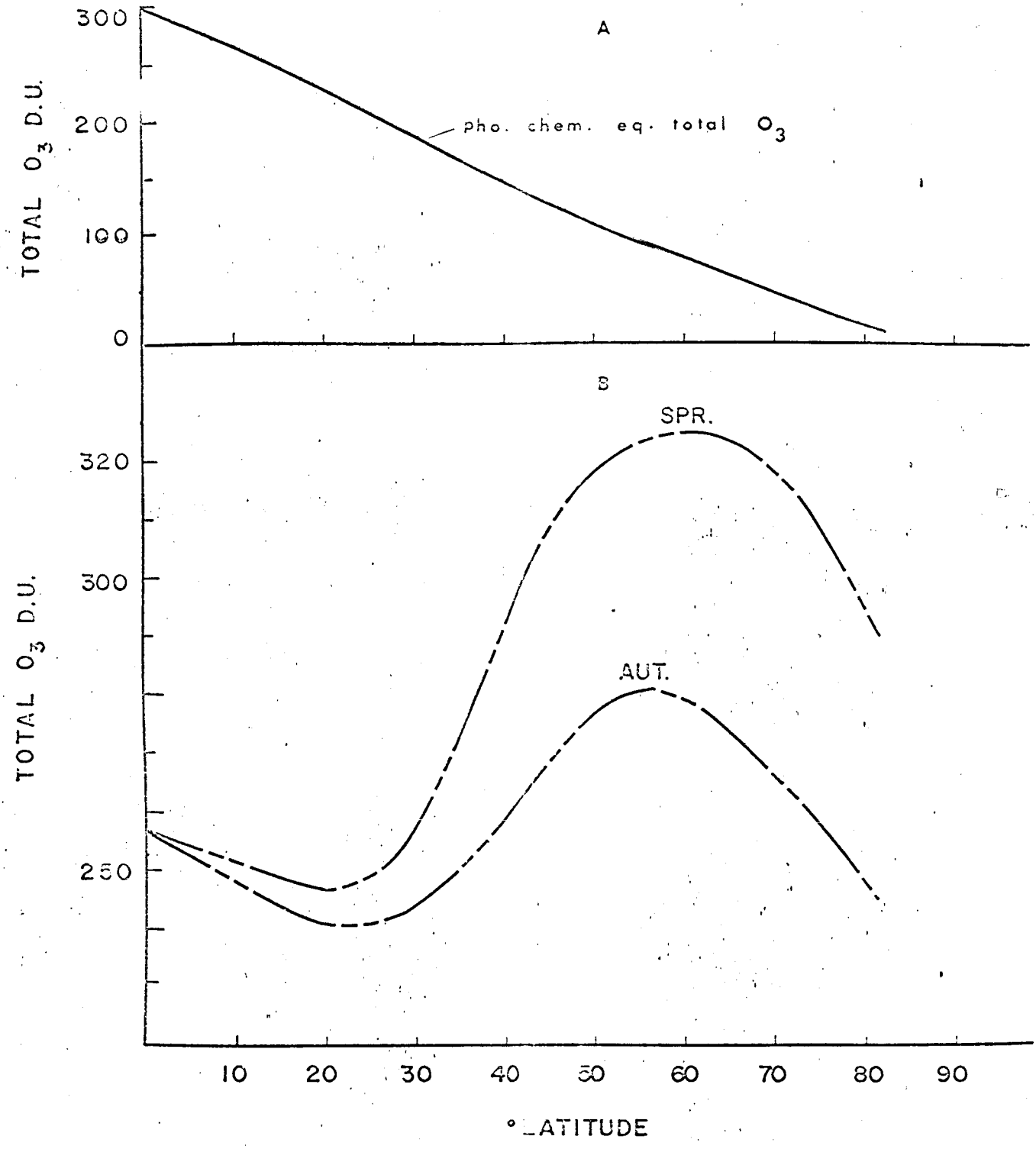

Fig. 15. Comparison between the total ozone variation with latitude obtained from pure photochemical theory (Fig. 12), and from the combined effects of photochemical and transport processes (Fig. 14).

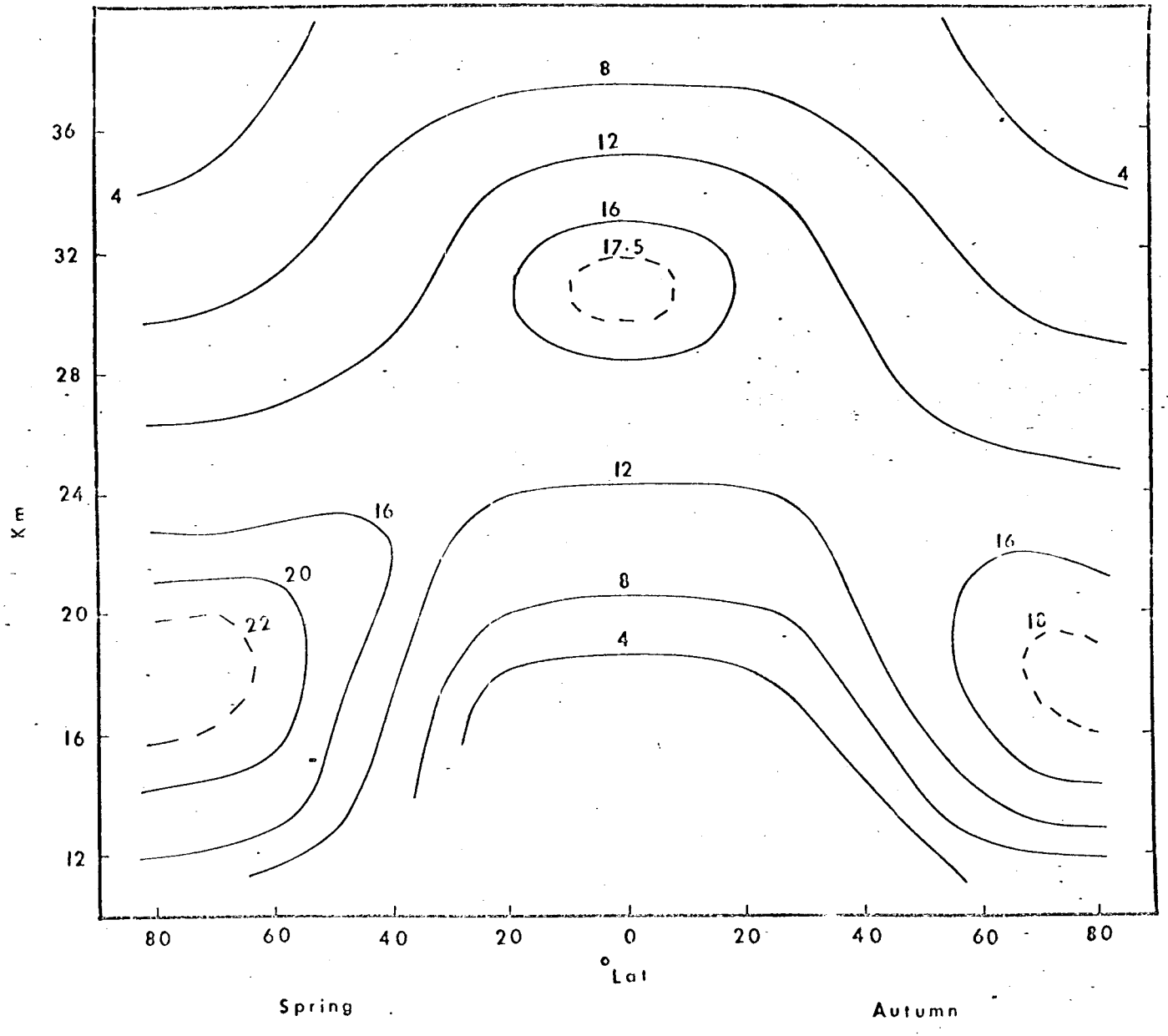

Fig. 16. Steady state distribution of ozone (D.U./km) computed for the equinoxes with K_z (Table 1) increasing with latitude, and 20% of Murgatroyd and Singleton's (1961) mean meridional circulation.

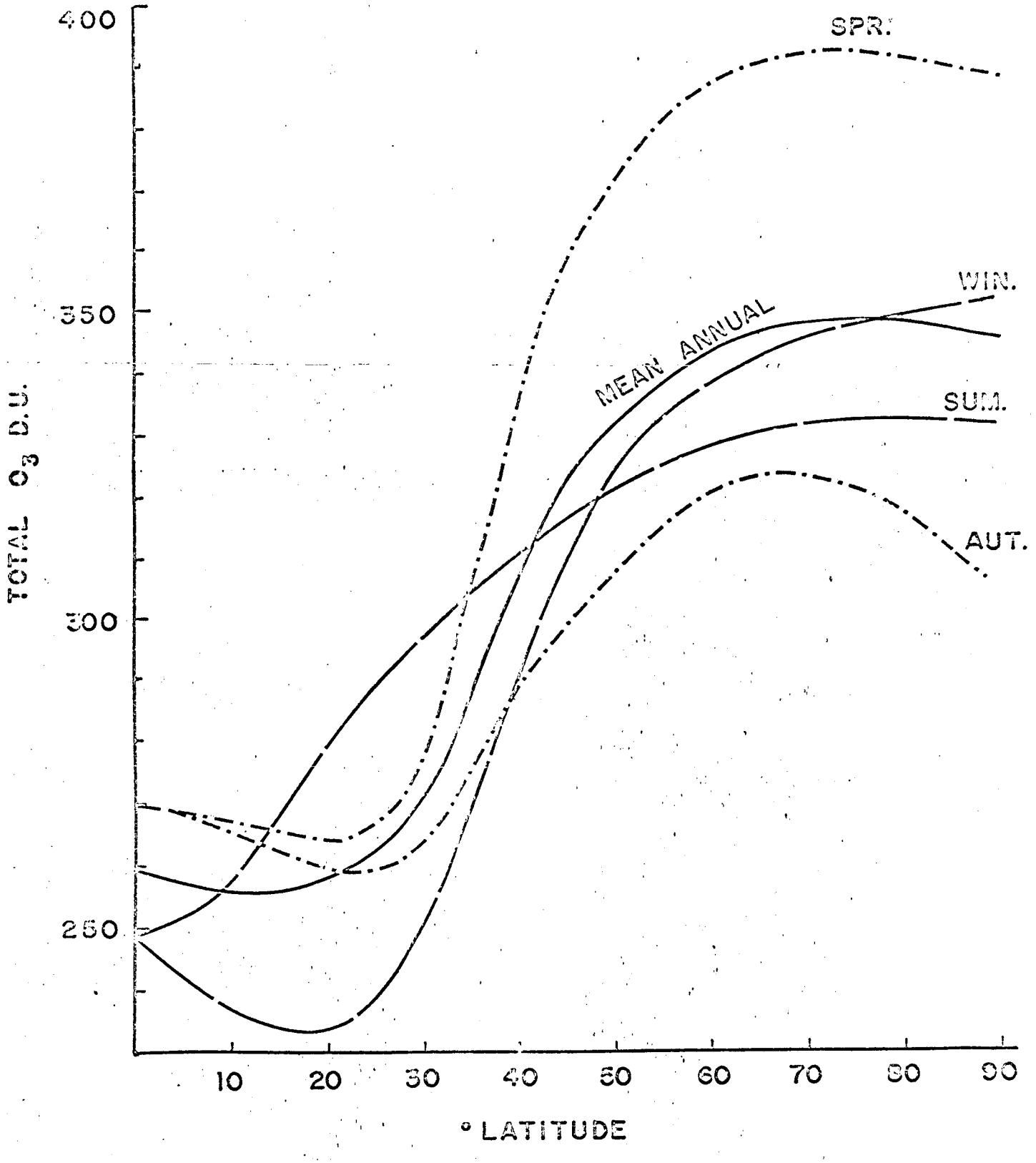

Fig. 17. Computed seasonal and latitudinal variation of total ozone corresponding to Figs. 16 and 18.

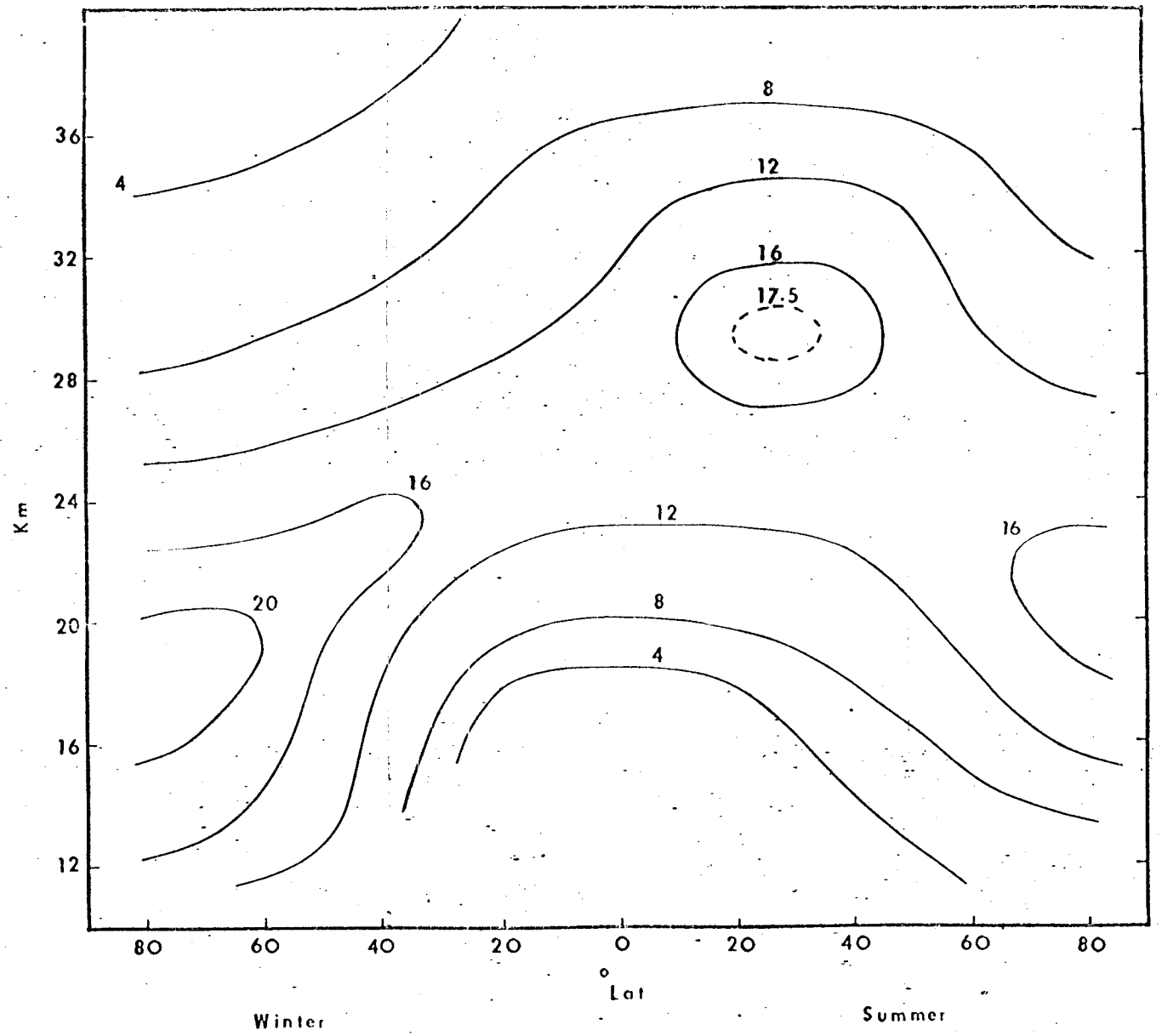

Fig. 18. Steady state distribution of ozone (D.U./km) computed for the solstices with K_y and K_z (Table 3) increasing from subsolar point, and 20% of Murgatroyd and Singleton's mean meridional circulation.

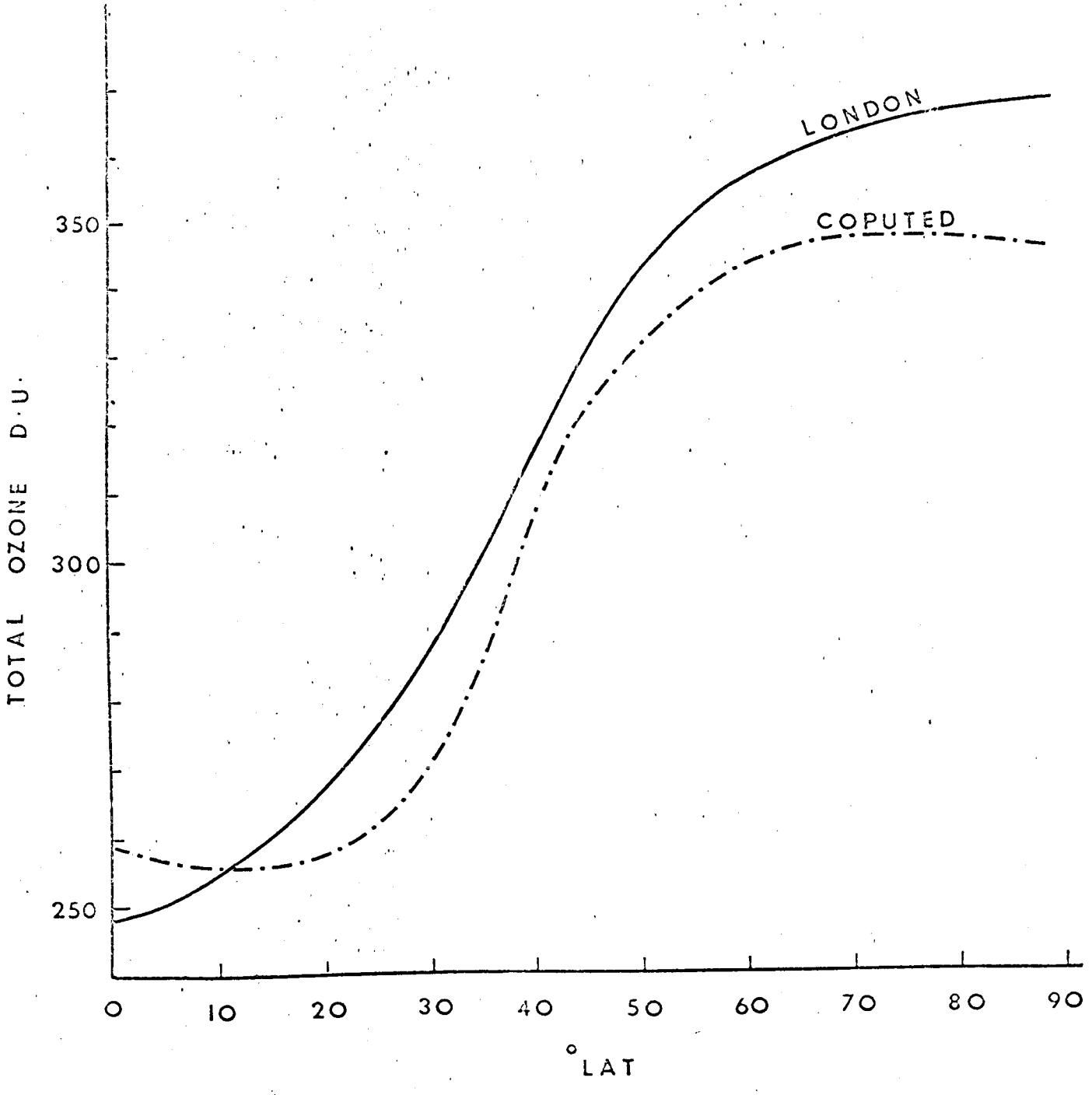

Fig. 19. Comparison of the computed mean annual (total ozone distribution with that of London (1962).

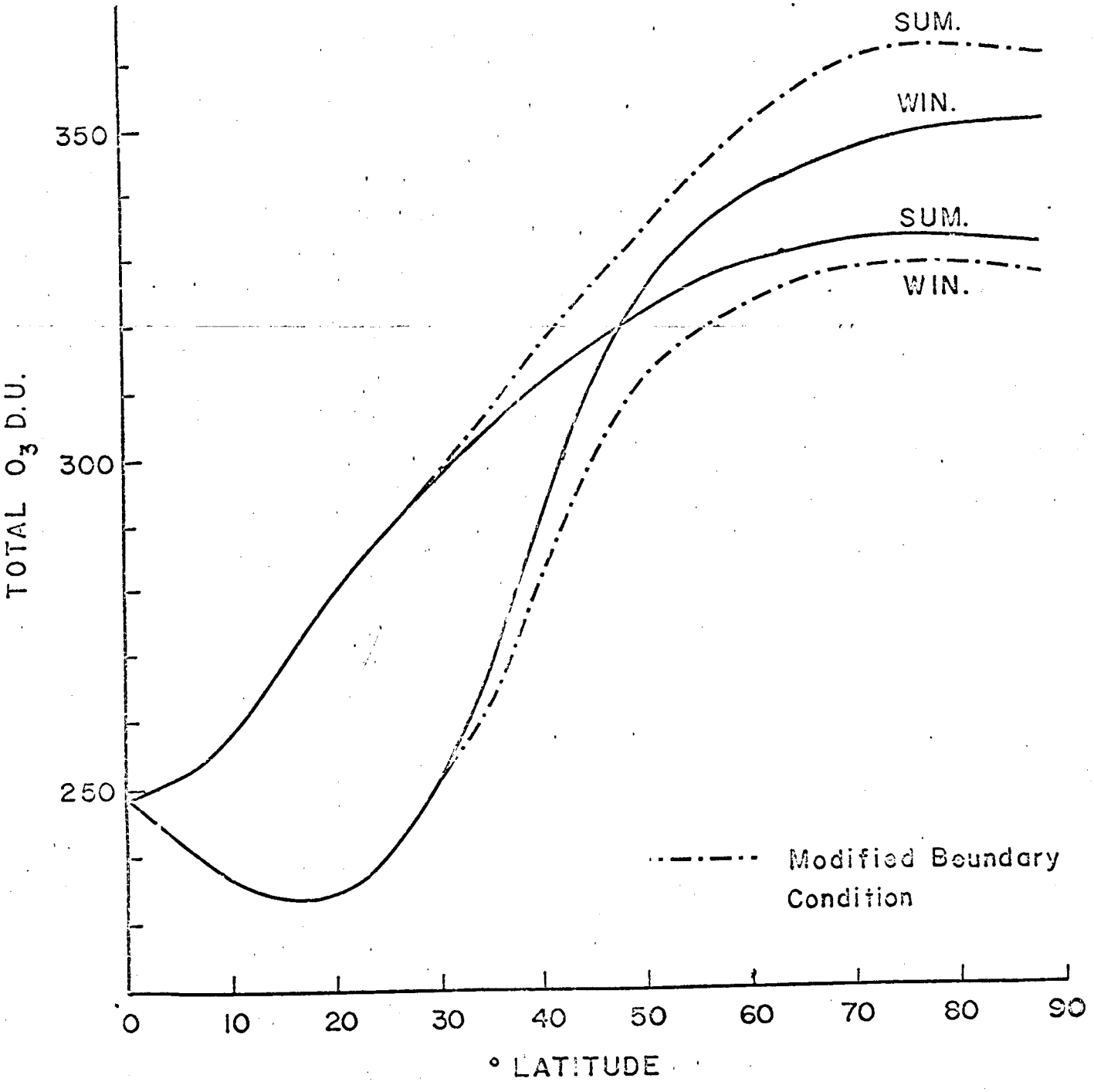

Fig. 20. Influence of the boundary condition at the tropopause on the computed total ozone.

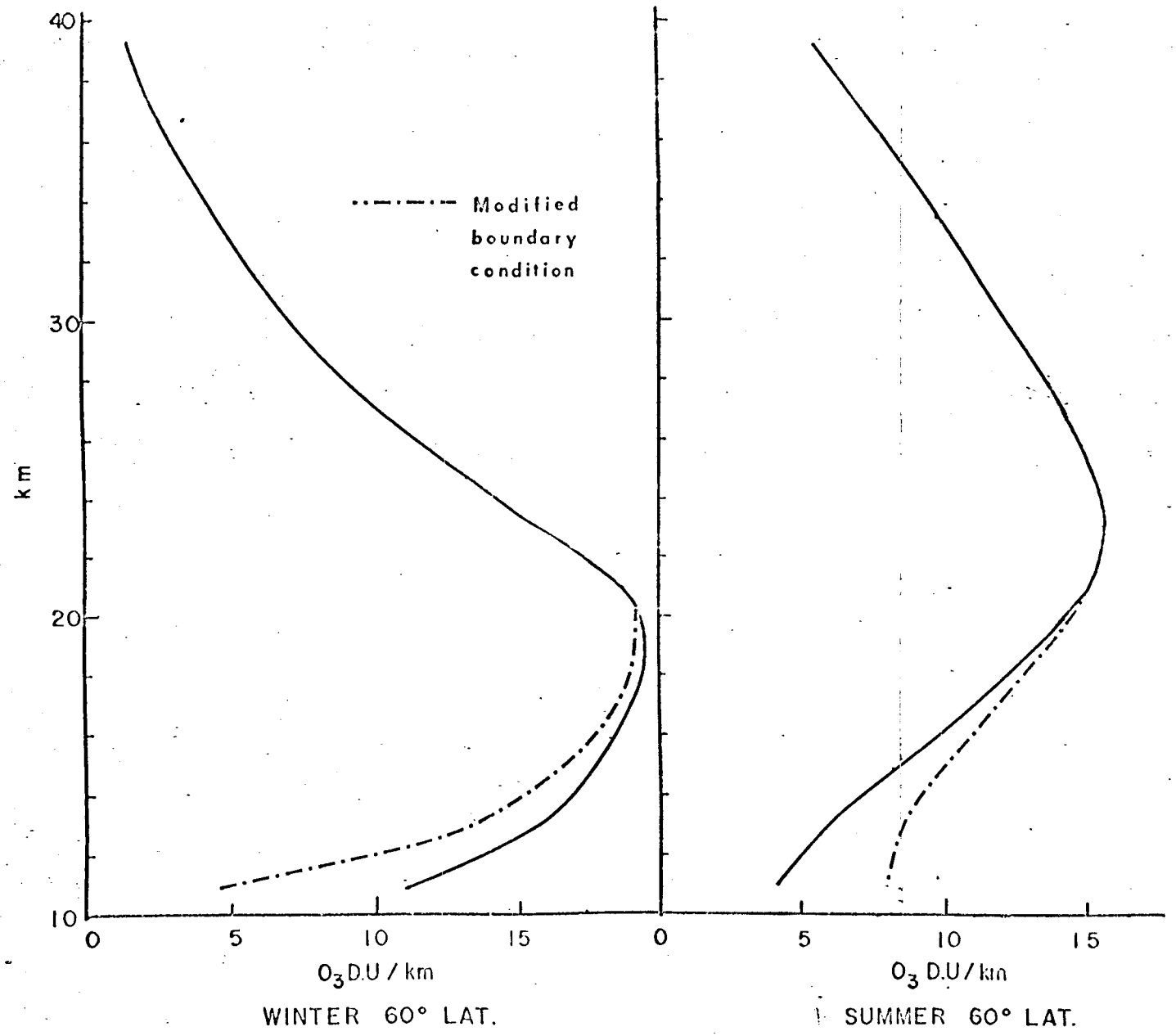

Fig. 21. Modification of the vertical distribution of ozone, at 60° latitude in the summer and winter hemispheres, produced by changing the boundary condition at the tropopause.